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SPECIAL STUDIES IN ELECTROLYSIS MITIGATION, No. 2

ELECTROLYSIS FROM ELECTRIC RAILWAY CURRENTS AND ITS PREVENTION—AN EXPERIMENTAL TEST ON A SYSTEM OF INSULATED NEGATIVE FEEDERS IN ST. LOUIS

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1. GENERAL DISCUSSION

INTRODUCTION

In a recent paper [1] the authors have discussed briefly the relative merits of some of the more important possible methods of electrolysis mitigation, and have drawn from that discussion the conclusion that insulated negative feeders should provide an economical and effective means of reducing electrolysis troubles to a practically negligible minimum. This discussion, however, was based mainly on theoretical considerations, and there has been

[1] Electric Railway Journal, Jan. 3, 1914.

up to the present time an almost complete dearth of quantitative experimental data bearing on the practical working out of systems of this character. While it is true that insulated feeders have been used abroad for many years, they have found no application in this country until within the last few years, and no comprehensive experimental data as to their operation has been published. Moreover, the feeder systems that have been used abroad have for the most part been used in connection with boosters, and the use of insulated feeders has usually been associated with the use of boosters in the minds of most engineers in this country. It is only natural, therefore, that engineers should be reluctant to install feeder systems of this character in the absence of any experimental data showing their effectiveness for accomplishing the purposes intended. It has, therefore, been necessary, in order to get adequate experimental data bearing on these problems, to install some experimental systems expressly for the purpose, and work of this sort has already been done in a few places, with the cooperation of electric railway companies. In making these installations localities were selected where conditions may be considered as normal and fairly representative of average conditions in American cities. The systems installed have been designed in accordance with the demands of service conditions, and are, therefore, of such nature that the experimental data obtained in connection with them is of a very practical character. Additional work of this kind is contemplated, and it is hoped through these investigations to accumulate evidence which will establish beyond doubt the practical possibilities of insulated negative feeder systems as a means of taking care of electrolysis troubles.

In connection with the general investigations that have been carried out by the Bureau of Standards for the past two or three years a considerable amount of preliminary work was done during the summer of 1912 in the city of St. Louis, as well as in other places. It was found that conditions in St. Louis were not exceptional, but that, in common with many other American cities, more or less trouble from electrolysis was experienced, and the tests showed that there was need for improvement in this direction. As a result of these preliminary tests a full report was

prepared by the engineers of the Bureau of Standards and submitted to the United Railways Co., of St. Louis. In that report the conditions as to danger from electrolysis were fully set forth, and recommendations were made for removing the cause of the damage.

In making these tests the engineers of the Bureau of Standards had the active cooperation of the officials of the United Railways Co., who furnished all necessary data in regard to track layout, feeder installations, car schedules, etc., which were required in order to design in detail a suitable system for the transmission of the current and its return to the power stations in a manner to take care of the traffic adequately and at the same time eliminate in a large measure future trouble from electrolysis. Based on these data and the experimental data obtained by the Bureau of Standards a thorough study of the whole situation was made, and the conclusion was arrived at that the best way to take care of electrolysis troubles was through the installation of insulated negative feeders.

When this report was submitted to the United Railways Co. an arrangement was made with them for the actual carrying out of the recommendations in the case of one of the substations of the company for the purpose of demonstrating the effectiveness of the proposed plan. The work of installing the negative feeders was done by the United Railways Co., and throughout the entire investigation the representatives of the Bureau of Standards had the cordial cooperation of the engineers and officials of the company, and the services of several of the company's men to assist in carrying on experimental work.

PURPOSE AND PLAN OF INVESTIGATIONS

The purpose of the test was twofold—first, to demonstrate the effectiveness of the insulated return feeder system as a means of mitigating electrolysis troubles; and, second, to determine the relative cost of securing equally good electrolysis conditions by the use of insulated and uninsulated negative feeders. In order to obtain data on the relative merits of the uninsulated and insulated systems it was necessary to install a system of negative feeders complete and in such a way that they could be converted into an

insulated or uninsulated feeder system at will. Since the negative feeders of the substation selected for the test were on poles or in fiber ducts, this could readily be accomplished by tying the bus bar to the tracks near the power house for the uninsulated system and removing such ties and inserting suitable resistance taps for the insulated system.

In both cases the feeders themselves were insulated from the tracks between the point at which they were tied into the tracks and the bus bar, but since in the uninsulated system the feeders were at the same potential as the tracks at both ends, the potential drops on the feeders were, of course, the same as the potential drops on the tracks which they parallel, and hence electrical conditions were substantially the same as they would be if the feeders had been uninsulated, and the relative electrolysis conditions and costs would also be identical. In the present case the tests were first made on the uninsulated feeder system; then suitable resistance taps were placed at the power house and at certain points out on the line to give proper distribution of current between the feeders, and the tests were repeated to show the change in conditions. A complete record of both of these series of tests is given below.

The station selected for this experimental investigation was the new Ann Avenue substation, located at the corner of Mississippi and Ann avenues. The rated capacity of this station is 4000 kilowatts at the present time, and the peak load (average for one hour) was at the time the tests were made about 7540 amperes. The average load for 24 hours was 3500 amperes, giving a load factor of about 46 per cent. It will therefore be seen that conditions at this station as regards size and character of the load are fairly representative of average conditions in a moderate-sized city substation. The track network in the district fed by the station is shown in Figs. 1 and 2. These show that only one single track passes immediately by the station, and another single track passes along the street one block to the east. This is therefore an unfavorable location with respect to returning the current to the station, because the cross section of rails approaching the station is unusually small. However, this was not the governing factor in determining the location of this station. On this account a

Fig. 1.—*Original negative feeder system, Ann Avenue district*

Fig. 2.—*Insulated negative feeder system, Ann Avenue district*

relatively large amount of copper would have to be installed in any case, whether the insulated or uninsulated system be used, and therefore the cost of returning current to this station, per kilowatt of capacity, would be expected to be considerably higher than the average, and this fact makes the test of the insulated system a more severe one from the economic standpoint, although it has no appreciable bearing on the effectiveness of the system in reducing electrolysis troubles.

The station in question is a new station which was just nearing completion at the time arrangements were made for the proposed tests. A considerable amount of negative copper was already in place, and in designing the proposed insulated feeder system this copper was allowed to remain; extensions were made where necessary and the current distribution was adjusted by means of resistance taps. The cross-sectional area of the feeders is not, therefore, just as it would have been if a new insulated feeder system had been installed throughout; and this also tends to make the cost run somewhat higher than would otherwise have been the case.

The original feeder layout designed by the engineers of the United Railways Co. for the negative return is shown in Fig. 1, and the system as finally completed for the insulated feeder layout is shown in Fig. 2. An examination of these two figures shows that changes were made in three cases.

In one case a feeder of 1 000 000 circular mils cross section had been designed to run from the negative bus eastward along Ann Avenue and tied to the tracks at both Eighteenth Street and Ann Avenue and Twelfth Street and Ann Avenue. The change made here was merely to remove the tie at Eighteenth Street and Ann Avenue and install a pair of 0000 cables running directly from the tracks at Eighteenth Street and Ann Avenue to the bus bar, thus giving two separate feeders to those two points instead of one common feeder. The length of each of these 0000 feeders was about 760 feet.

A second change will be noted on Gravois Avenue. The original feeder layout contemplated running one feeder of 1 000 000 circular mils to Victor Street and Gravois Avenue, and another to Jefferson and Gravois avenues. The feeder at Jefferson and Gravois avenues was allowed to remain, but the feeder running to Victor

Street was cut loose from the tracks at this point and extended to California and Gravois avenues, a distance of about 2300 feet.

The third extension was in one of the feeders running north on Mississippi Avenue. The original plan contemplated running one 1 000 000 circular mil cable to Mississippi and Geyer avenues and a similar cable to Mississippi and Lafayette avenues. A resistance was put in series with the feeder extending to Geyer Avenue, and the Lafayette Avenue feeder was extended to Lafayette Avenue and Grattan Street, and a resistance was inserted in the tap to Mississippi and Lafayette avenues. The amount of copper added in extending the feeder from Mississippi Avenue to Grattan Street was 1300 feet of 1 000 000 circular mil cable. The total weight of copper added in the three places was therefore about 12 113 pounds. The original plan called for the installation, in addition to the above-mentioned feeders, of a 1 000 000 circular mil cable running east on Ann Avenue to Ninth Street, a distance of 2900 feet, and two 1 000 000 circular mil feeders running east from the power house along Ann Avenue to Broadway, a distance of 3800 feet. The total weight of copper under the original plan would have been 60 100 pounds, all of it in 1 000 000 circular mil cables, while in the system as actually completed there were, as is shown later, 72 213 pounds of copper, all of which was of 1 000 000 circular mils cross section except the two short 0000 feeders running to Eighteenth Street and Ann Avenue. The excess cost of the actual system over that of the original system was about $3147, exclusive of the cost of the resistances which is negligible, figuring the cost of overhead feeders at $750 per 1000 feet of 1 000 000 circular mil cable installed. All of the additional feeders were installed overhead, except the two 0000 cables, which were in fiber conduit. The cost of the latter feeder is figured at $1400 per 1000 feet of million circular mils of cable.

In designing these extensions the object was to reduce the potential gradient in the rail return at all points of the system to a value not exceeding 1 volt per 1000 feet, average for one hour at peak load, which at 46 per cent load factor would correspond to an average of about 0.46 volt per 1000 feet during the 24-hour period. In making the tests the system was first arranged as an uninsulated feeder system by tying the tracks at Mississippi and Ann avenues

and Eighteenth Street and Ann Avenue as directly to the bus-bar as the connecting cables would permit. A complete electrical survey was then made to determine the electrical conditions existing in the negative return and pipe systems. These measurements include the following:

1. *Rail-Gradient Measurements.*—These for convenience comprised measurements with a millivoltmeter of the drop of potential on a fixed length of 4 feet of rail, the measurements on all the rails on any particular street being taken at each point. This method involves the assumption that all joints are as good as equivalent length of rail. Numerous preliminary tests of joints were made to determine the condition of the joints and all bad joints found were repaired before final measurements were begun.

2. *Current Flow in Pipes, Including Both Gas and Water Mains.*—For this purpose excavations were made at a number of points and rubber-covered leads were fastened to the pipes 4 feet apart, the leads being brought underground to service boxes located inside the curb. These points were for the most part located within a half-mile of the station. Measurements of the millivolts drop on the pipe at these points permit the calculation of the actual value of the current flow in the pipes at those points, the size and kind of pipe being known. In addition to these, potential measurements were made between adjacent fire plugs at a number of outlying points considerably beyond the terminals of the feeders. While these do not permit the calculation of the actual current flow in those localities the measurements taken under the insulated and uninsulated systems gave values proportional to the current flow under the two conditions, and thus afford a means of determining the relative current flow in the two cases.

3. *Potential Difference Measurements Between Pipes and Rails.*—These measurements were taken throughout a large part of the area affected by the station, including a considerable portion of the region where the pipes were negative to the rails, in order that any tendency of the insulated feeder system to extend the positive area could be determined.

4. *Over-all Potential Measurements.*—These measurements were made between a point on the rails adjoining the power house and a number of remote points near the extreme limits of the feeding districts. These measurements were made with the coöperation

of the Kinloch Telephone Co., which connected the telephone wires to the points at which potential measurements were desired, so that the measurements could all be made at the telephone exchange.

5. *Current in the Various Feeders.*—These data were taken in order to determine the correctness of the current distribution and the economy with which the copper was being worked in the different parts of the system.

After all of the above measurements were completed the system was converted into an insulated feeder system, as mentioned above, and the same measurements repeated at the same points. In taking the electrical measurements at any one point the readings were taken every 15 seconds for a period varying from 5 to 15 minutes, according to local conditions, and the average of all these readings is taken as the reading at that particular time of day.

Since readings at different points were necessarily taken at different hours of the day, when the station load differed, the readings as observed are not directly comparable, and in order to get a basis on which the readings under different conditions could be directly compared it was found most satisfactory to reduce all the readings to the average 24-hour values. This was done by dividing the average observed reading at any point by the ratio of the station load at that particular time of day to the 24-hour average station load. It is this reduced 24-hour average value that is recorded in the tables in each instance. Careful study of a large amount of test data shows that this affords a very satisfactory basis of comparison.

In converting to the insulated feeder system, the different extensions outlined in detail above were installed and the feeders were adjusted for approximately equal drop by the insertion of suitable resistances where necessary. The number and location of these resistances are shown in Fig. 2, which gives the final layout of the insulated feeders. It will here be seen that there are three resistances at the substation in the cables running to the tracks at Mississippi and Ann avenues, Eighteenth Street and Ann Avenue, and Twelfth Street and Ann Avenue. There is also a resistance in the feeder running north on Mississippi Avenue to Mississippi and Geyer avenues, the resistance being at the outer end of the feeder. The feeder running north on Mississippi Ave-

nue to Lafayette Avenue is connected to the tracks at Lafayette and Mississippi avenues through a resistance tap designed to give about 4 volts drop at peak load. There is also a resistance tap at Ann Avenue and Ninth Street. This is not, however, in series with any feeder, but is connected between the feeder which is connected to the tracks at Ninth Street and the two feeders which run on to Broadway. It, therefore, affords a certain measure of paralleling between these feeders.

A comparison of the measurements taken under the insulated and uninsulated feeder systems shows clearly the relative danger from electrolysis under the two systems. Although the amount of copper in the feeder systems under these two series of tests is not the same in each case, the difference was not great enough to produce any marked change in electrolysis conditions under the uninsulated feeder system. This was shown in advance by careful calculations and was borne out by experimental data obtained later, so that although some copper was added for the insulated feeder system, such copper, because of its outlying location, would have exerted practically no influence when used in connection with the uninsulated system. The results show the changes due to conversion from an uninsulated to an insulated system with substantially the same amount of copper.

2. RAIL GRADIENTS

In determining the rail gradients measurements were taken on a fixed length of 4 feet of rail. The points for measurement were selected so as to give the maximum gradients that existed in each case. This means that gradient measurements were taken on all sides of each point at which a negative cable was tapped to the tracks under both the insulated and uninsulated feeder systems. It is obvious that at more remote points the gradients tend to become less than the values recorded at these places, except under very special conditions, which did not exist in this installation. The value of these rail gradients consists chiefly in that they permitted the determination of whether or not the gradients calculated in advance had been approximately realized, and they also afforded a definite indication as to the condition of the track. Since the gradients were measured on all of the rails on a given street, if the tracks were in good condition and properly cross bonded, the

rail-gradient measurements should be substantially equal on all of the rails. If, however, there was a marked difference in gradients on different rails, it indicated that the current was not equally distributed between the rails, which in turn indicated a bad condition of the joints somewhere in the vicinity. The latter was found actually to be the case, and it was necessary to make a considerable number of repairs of the track before satisfactory conditions were finally realized. The location of the points at which potential gradient measurements were taken, and also the values obtained under both the insulated and uninsulated systems, are shown in Table 1.

TABLE 1

Rail Gradients

Location	Uninsulated feeders		Insulated feeders	
	Direction of flow	Gradient volts per 1000 feet	Direction of flow	Gradient volts per 1000 feet
Grattan north of Lafayette			South	0.47
Lafayette east of Grattan			West	0.15
Lafayette west of Grattan			West	0.34
Lafayette east of Mississippi	West	1.90	West	0.59
Lafayette west of Mississippi	East	0.16	East	0.48
Mississippi north of Lafayette	South	0.90	South	0.72
Mississippi south of Lafayette	South	1.87	South	0.75
Mississippi south of Geyer	South	2.89	South	0.57
Geyer east of Mississippi	West	0.91	West	0.29
Geyer west of Mississippi	East	1.17	West	0.60
Mississippi south of Ann	North	1.35	North	0.21
Gravois south of Victor	North	1.77	North	0.17
Victor east of Gravois	East	0.29		
Gravois west of Jefferson	East	0.98	East	0.03
Jefferson north of Gravois	South	0.69	South	0.68
Jefferson south of Gravois	North	0.44	North	0.22
Gravois west of California			East	0.59
California north of Gravois			South	0.33
California south of Gravois			North	0.15
Broadway north of Ann	South	0.59	South	0.44
Broadway south of Ann	North	0.35	North	0.90
Ninth north of Ann	South	0.69	South	1.20
Ninth south of Ann	North	0.14	North	0.39
Twelfth north of Ann	South	0.33	South	0.25
Twelfth south of Ann	North	0.80	North	0.30
Eighteenth north of Ann	South	0.60	South	0.80
Eighteenth south of Ann	North	0.75	North	0.43
Average		0.93		0.46

By comparing the figures point by point in the columns showing average gradients under each system we get the effect produced by the change from uninsulated to insulated feeders. An examination of these columns shows that in many places the gradients have been greatly reduced, this being particularly true in the region near the power house where the gradients were rather high under the uninsulated system.

It will be noted that there is but one point which shows a potential gradient greater than 1 volt per 1000 feet under the insulated feeder system, whereas the average of all points is but 0.46 of a volt. Since the station-load factor is about 46 per cent, this means that the average potential gradient at peak load is almost exactly 1 volt, and most of the readings will not vary much from this mean value. These figures show that the installation of the insulated return feeder system has substantially fulfilled the conditions that it was designed to accomplish in the way of potential gradients, in that the mean value at peak load does not exceed the calculated value of 1 volt per 1000 feet. Under the uninsulated feeder system, however, there are a considerable number of readings which run above 1 volt average, the highest being 2.89 volts per 1000 feet, which corresponds to a peak-load value of about 6.2 volts per 1000 feet. The average for all points under the uninsulated feeder system is 0.93 volt for the 24-hour period, which corresponds to a mean value of 2 volts during peak load.

While it is important that rail gradients should be kept low, this figure is only of indirect importance, since low gradients in general mean small leakage and consequently reduced current flow on the pipes. Of even greater importance, however, than low gradients is the direction of the gradient. Under the uninsulated feeder system this gradient is necessarily continuous from the outlying districts clear into the power house; whereas, under the insulated feeder system, the current flow can, if desired, be made to flow from all directions toward the points of tap of the insulated feeders to the rails, and since these points are distributed through a considerable portion of the feeding area, the direction of current flow in the rails can be frequently reversed, so that the gradient in any one direction will extend over only a compara-

tively short distance, and hence large differences of potential between different points in the earth can not be set up.

It will be evident, therefore, that the improvement in electrolysis conditions caused by the installation of insulated feeders will in general be much greater than the ratio of reduction of the rail gradients. This is borne out in a very marked manner by the data given below.

3. CURRENT FLOW IN PIPES

One of the best criteria for determining the relative amounts of damage from electrolysis under different conditions of track return is afforded by determining the current flow in the pipes. Since, as in the present case, where there were no metallic connections to pipes, all the current flow carried by the pipes must ultimately be discharged into the earth, the total amount of electrolysis will be approximately proportional to the current flow on the pipes.

Table 2 shows the current flow, as measured at a number of points under the insulated and uninsulated feeder systems. The currents in all cases were calculated from measurements of millivolt drop on a 4-foot length of pipe, the resistance of the pipe being determined from the size and kind of pipe and known constants as determined from numerous laboratory tests. This method of determining current in the pipes, while not strictly accurate, because of variations in the kind and weight of the pipes, has, nevertheless, been shown to be sufficiently accurate for most practical purposes when used with care.

Referring to Table 2, the first column, headed "Location," gives the points at which current measurements were made; the second column, headed "Size of pipe," gives the diameter in inches of the pipe on which the current was measured, and in each case this figure is followed by the letter W or G, indicating whether the pipe was a gas or water main. In the third and fourth columns the current flow average for the 24-hour period is given for the two systems.

TABLE 2

Current in Gas and Water Pipes. Not Drained

Location	Size of pipe, inches	Current in amperes	
		Uninsulated system	Insulated system
Russell, west of Thirteenth	30 W	46.80	3.78
Russell, west of Mississippi	6 W	0.60	0.00
Ann, west of Twelfth	4 G	0.16	0.17
Ann, west of Eighteenth	6 W	3.24	1.86
Ann, east of Mississippi	4 G	6.93	2.16
Ann, east of McNair	6 W	2.35	0.05
Ann, east of McNair	4 G	0.17	0.03
Gravois, west of Eighteenth	6 W	11.80	1.63
Gravois, west of Shenandoah	4 G	0.08	0.03
Shenandoah, west of Thirteenth	20 W	9.42	0.62
Shenandoah, east of McNair	20 W	43.10	12.50
Lynch, west of Indiana	6 G	0.15	0.11
Eighteenth, north of Shenandoah	6 W	6.97	3.62
Eighteenth, north of Victor	20 W	23.40	7.48
Lemp, north of Victor	6 G	0.11	0.05
Mississippi, south of Lafayette	6 G	0.06	0.03
Mississippi, south of Allen	20 W	1.40	1.70
Mississippi, south of Russell	20 W	56.40	19.30
Mississippi, south of Ann	20 W	19.60	3.06
Salena, north of Shenandoah	20 W	40.20	7.02
Salena, north of Victor	6 W	0.31	0.10
Total		273.25	65.30

An examination of the columns headed "Current in amperes" shows that there has been a very marked reduction in the current flow in practically all cases. The general average ratio of reduction is best determined by summing up the total current flow in the pipes at all points and determining the ratio of these total currents under the insulated and uninsulated systems. It will be seen from these figures that the total current flow at all observation points under the uninsulated feeder system was 273.3 amperes, whereas the corresponding figure under the insulated feeder system was 65.3 amperes, which gives an average ratio of reduction of about 4.2 to 1. This represents the average reduction in the rate of electrolytic corrosion throughout the system, as indicated by these

measurements. In some localities, particularly near the power station, the reduction will be greater than this, whereas in the more remote districts it will be correspondingly less, but these figures may be taken as a fair indication of the general improvement that is effected by the insulation of the feeders.

EFFECT OF PIPE DRAINAGE ON CURRENT FLOW IN PIPES

While no attempt was made in the present investigation to install a complete pipe-drainage system, it was deemed worth while to temporarily tie in the pipes at points near the station in order to determine the effect of such tying in on the general magnitude of current flow in the pipes, and particularly the relative increase of current produced by such tying in under the insulated and uninsulated feeder systems. For this purpose temporary ties between the water and gas pipes at Mississippi and Ann Avenues and the tracks were installed, and likewise a direct tie between the water pipes and tracks at Twelfth Street and Ann Avenue was installed.

Measurements of current flow at the same places as shown in Table 2 were made with the pipes thus tied in and with the feeders insulated and uninsulated from the ground. The results of these measurements are shown in Table 3. Here the columns have the same significance as in Table 2, the columns 3 and 4 representing the currents in the pipes under the uninsulated and insulated feeder systems, respectively. It will be seen by comparing these figures with those of Table 2 that there has in general been a marked increase in current flow in the pipes, and this is particularly true in the case of the uninsulated system.

The sum of all the currents at different points of measurement is 844 amperes for the uninsulated system and 84.8 amperes under the insulated system, showing that under these conditions of tying in the current flow in the uninsulated system is, on the average, about 10 times as great as under the insulated feeder system. It will also be observed by comparing the totals of Table 2 with those of Table 3 that the tying in of the pipes with the uninsulated feeder system causes an increase in the current flow in the ratio of about 3.1 to 1, whereas under the insulated feeder system the increase in current due to tying the pipes in is increased only in the ratio of 1.3 to 1.

TABLE 3

Current in Gas and Water Pipes. Pipes Drained

Location	Size of pipe, inches	Current in amperes	
		Uninsulated system	Insulated system
Russell, west of Thirteenth	30 W	108.00	5.02
Russell, west of Mississippi	6 W	4.90	0.71
Ann, west of Twelfth	4 G	0.24	0.32
Ann, west of Eighteenth	6 W	5.04	3.15
Ann, east of Mississippi	4 G	9.20	3.53
Ann, east of McNair	6 W	4.79	0.05
Gravois, west of Eighteenth	6 W	21.63	1.98
Ann, east of McNair	4 G	0.34	0.35
Gravois, west of Shenandoah	4 G	0.30	0.08
Shenandoah, west of Thirteenth	20 W	8.82	2.20
Shenandoah, east of McNair	20 W	83.00	20.60
Lynch, west of Indiana	6 G	0.11	0.11
Eighteenth, north of Shenandoah	6 W	9.26	3.37
Eighteenth, north of Victor	20 W	42.80	2.57
Lemp, north of Victor	6 G	0.10	0.05
Mississippi, south of Lafayette	6 G	0.11	0.05
Mississippi, south of Allen	20 W	8.17	1.20
Mississippi, south of Russell	20 W	301.00	22.20
Mississippi, south of Ann	20 W	105.40	6.94
Salena, north of Shenandoah	20 W	128.40	10.23
Salena, north of Victor	6 W	2.55	0.11
Total		844.16	84.82

This shows that the tying in of the pipes has a much smaller tendency to increase the current flow in the case of insulated feeders than it has in the case of uninsulated feeders. The total current flow with the pipes tied in under the insulated-feeder system is only 84.8 amperes, whereas the current flow under the uninsulated system with the pipes not tied in is 273 amperes, which means that draining the pipes at these two points under the insulated-feeder system results in only thirty-one per cent as much current flowing in the pipes as the flow in the pipes without such drainage under the uninsulated-feeder system.

These various ratios are summarized in Table 4 and show in a very striking manner the marked reduction in current flow that in every case accompanies the insulated-feeder system, and they

form an excellent illustration of the value of the insulated feeders as against the uninsulated-feeder systems as a means of reducing electrolysis trouble.

TABLE 4

Summary of Current in Pipes and Current Flow Ratios

CURRENT IN PIPES

	Amperes
Uninsulated system, pipes drained, total current	844.1
Uninsulated system, pipes not drained, total current	273.2
Insulated system, pipes drained, total current	84.8
Insulated system, pipes not drained, total current	65.3

CURRENT FLOW RATIOS

$$\frac{\text{With insulated feeders}}{\text{With uninsulated feeders}} = \frac{\text{Pipes not drained}}{\text{Pipes drained}} = \frac{65.3}{273.2} = 0.239 \qquad \frac{84.8}{844.1} = 0.101$$

$$\frac{\text{With pipes drained}}{\text{With pipes not drained}} = \frac{\text{Insulated feeders}}{\text{Uninsulated feeders}} = \frac{84.8}{65.3} = 1.30 \qquad \frac{844.1}{273.2} = 3.09$$

$$\frac{\text{Insulated feeders, drained pipes}}{\text{Uninsulated feeders, pipes not drained}} = \frac{84.8}{273.2} = 0.31$$

The above figures show the current flow in the pipes in the region within approximately a quarter of a mile radius of the power station. It was deemed advisable also to determine the relative current flow under the different conditions at points more remote from the power house, and for this purpose, in order to avoid the labor of additional excavations, potential measurements were made between adjacent fire hydrants at suitable places, the potential differences under the insulated and uninsulated systems being taken as representing the relative current flow in the two cases. Under each feeder system also these measurements were taken with the pipes drained at the two points mentioned above near the station, and also with the pipes not drained, so as to show the tendency, if any existed, of pipe drainage to increase current flow in the pipes at very remote points. These data are given in Table 5.

TABLE 5

Potential Differences Between Fire Plugs

Location			Average volts			
			Uninsulated feeders		Insulated feeders	
On—	From—	To—	Pipes not drained	Pipes drained	Pipes not drained	Pipes drained
Mississippi	Kennett	Lafayette	0.685	0.908	0.042	0.059
Mississippi	Allen	Geyer	.211	.425	.150	.137
Gravois	Sidney	Victor	.646	.735	.229	.260
Ann	Menard	Eleventh	.320	.624	.159	.208
Ann	Jefferson	Indiana	.132	.308	.060	.023
Shenandoah	Indiana	Missouri	.394	.648	.159	.219
McNair	Lynch	Sidney	.156	.333	.001	.007
Total			2.544	3.983	0.800	0.913

POTENTIAL DIFFERENCE RATIOS

$$\frac{\text{With insulated feeders}}{\text{With uninsulated feeders}} = \frac{\text{Pipes not drained}}{\text{Pipes not drained}} = \frac{0.800}{2.544} = 0.314$$

$$\frac{\text{With insulated feeders}}{\text{With uninsulated feeders}} = \frac{\text{Pipes drained}}{\text{Pipes drained}} = \frac{0.913}{3.983} = 0.229$$

$$\frac{\text{With pipes drained}}{\text{With pipes not drained}} = \frac{\text{Uninsulated feeders}}{\text{Uninsulated feeders}} = \frac{3.983}{2.544} = 1.56$$

$$\frac{\text{With pipes drained}}{\text{With pipes not drained}} = \frac{\text{Insulated feeders}}{\text{Insulated feeders}} = \frac{0.913}{0.800} = 1.14$$

$$\frac{\text{Insulated feeders, drained pipes}}{\text{Uninsulated feeders, pipes not drained}} = \frac{0.913}{2.544} = 0.359$$

In this table are shown the voltage drops between hydrants, under both the insulated and uninsulated feeder systems, and under each system are shown also the voltage drops with the pipes drained and not drained. The ratio of the sums of the voltage drops with the insulated and uninsulated systems is 0.314 with the pipes not drained. Under pipe drainage the difference is still more marked, the ratio of the sums of the volt drops being here only 0.229. With the insulated feeder systems the ratio of current flow with the pipes drained and not drained is 1.14. With the uninsulated feeder system the ratio is 1.56, indicating that even in these more remote points the current flow shows a marked increase when the pipes are tied in, but that this increase is much less marked in the case of the insulated feeder system than it is in the case of the uninsulated feeder system. The last ratio given in

the summary of Table 5 also shows that at these outlying points the current flow in the pipes, under the insulated feeder system combined with pipe drainage at the points near the power house, is but little over a third of the current flow without pipe drainage under uninsulated feeder systems.

We wish to emphasize here the fact that in making the above tests with the pipes tied in, no attempt was made to install a scientific pipe drainage system with a view of obtaining minimum current flow in the pipes. If this had been done, the current flow under pipe drainage could no doubt have been materially reduced, particularly at points near the power house, but such reduction would not have occurred in the outlying points referred to under Table 5. The results as presented, however, while they do not show conditions that would exist under an ideal pipe drainage system, show, nevertheless, the tendencies which exist, and that conditions in regard to current flow in the pipes are invariably much better under the insulated feeder system than under the uninsulated system.

One point of special interest in connection with the data on current flow in the pipes should be mentioned here. By reference to Tables 2 and 3 it will be noted that those points marked W in column 2, indicating water mains, show in general a much higher current flow than the points marked G, which indicate gas mains. The reason for this is that the gas mains in this vicinity have a considerable number of cement joints, and this undoubtedly is responsible for the comparatively low current flow. It is probable that those points which show almost no current flow are sections which contain cement joints, whereas those points that show small yet appreciable current flow are older and lead-jointed sections, since both kinds are known to exist in this territory.

4. POTENTIAL DIFFERENCES BETWEEN PIPES AND RAILS

Another criterion for determining the relative danger to pipes under different conditions is the potential differences between pipes and rails. Such measurements do not give altogether reliable indications as to relative danger when made in different localities, because of differences in soil resistance and other local conditions, but when such measurements are made at the same

points under different physical conditions of the negative return the values afford an accurate measure of the relative danger from electrolysis. Such potential difference measurements were, therefore, made between fire hydrants and rails at a considerable number of points under both the insulated and uninsulated feeder systems, and the results are given in Table 6.

TABLE 6

Potential Differences Between Pipes and Rails

A. POTENTIALS ORIGINALLY OVER ONE VOLT

Location	Potential difference		Location	Potential difference	
	Uninsulated system	Insulated system		Uninsulated system	Insulated system
Twelfth and Russell...	1.80	0.70	Mississippi and Allen..	3.45	0.37
Eighteenth and Geyer..	1.38	0.29	Mississippi and Russell.	4.22	0.17
Eighteenth and Allen...	2.02	0.67	Mississippi and Gravois.	3.60	0.16
Eighteenth and Russell.	3.00	0.24	Gravois and McNair....	3.20	−0.84
Eighteenth and Ann....	2.15	0.08	Gravois and Victor.....	1.13	0.53
Eighteenth and Shenandoah.....	2.02	0.70	McNair and Geyer.....	1.91	0.15
Eighteenth and Victor..	1.69	0.55	Average.....	2.44	0.33
Mississippi and Geyer..	2.63	0.86			

Ratio of average values=7.4.

B. POTENTIALS ORIGINALLY LESS THAN ONE VOLT

Ninth and Lafayette....	0.62	0.02	McNair and Victor.....	0.94	0.52
Twelfth and Shenandoah.....	0.56	0.59	Salena and Victor.....	0.71	0.40
Grattan and Lafayette...	0.25	0.30	Jefferson and Lafayette..	0.22	−0.01
Eighteenth and Lafayette.....	0.38	0.05	Jefferson and Geyer....	0.06	−0.04
Eighteenth and Sidney..	0.69	0.25	Jefferson and Ann.....	0.00	−0.01
Mississippi and Lafayette.....	0.62	0.37	Jefferson and Gravois...	0.77	0.77
Lemp and Victor.....	0.71	0.35	Jefferson and Pestalozzi.	0.39	0.32
			Average decrease..	0.49	0.28

Ratio of average values=1.75.

C. POTENTIALS ORIGINALLY NEGATIVE

Broadway and Victor...	−0.70	+0.48	Grattan and Park.....	−0.51	+0.35
Broadway and Russell..	−0.01	+0.80	California and Geyer....	−0.01	+0.29
Ninth and Russell.....	−0.23	+0.80	California and Gravois..	−0.33	+0.84
Ninth and Victor.....	−0.33	+0.62	Average.....	−0.31	+0.56
Eleventh and Park.....	−0.37	+0.33			

An examination of these data reveals that for the most part there has been a marked reduction in potential differences, particularly in the region near the power house where such potential differences were originally high. In order to facilitate the interpretation of these data they have been divided into three groups with subheads A, B, and C. The data for all points at which original potential differences were greater than 1 volt are placed in group A; all those at which the pipes were positive but less than 1 volt are placed in group B; and all those points at which the pipes were originally negative but have become somewhat positive under the insulated feeder system are placed in group C.

On examination of group A, which includes the points of high original potential and therefore covers the area in which the original danger was greatest and the need for improvement most urgent, we find that there has been a very large reduction of potential differences between pipes and rails. In one case, notably at Gravois and McNair avenues, where the pipes were originally strongly positive to rails, they have become slightly negative, and in all the other points in this group a marked reduction is apparent. The average potential difference at all points under the uninsulated system was 2.44 volts, whereas under the insulated feeder system this average was reduced to 0.33 volt, giving a mean ratio of reduction of 7.4 to 1.

Referring to group B, where the original potential differences were less than 1 volt, we find there is still a very considerable reduction. The average for all of these points is 0.49 volt, whereas the average for the corresponding points under the insulated feeder system is 0.28 volt, giving a ratio of reduction of 1.75 to 1. Even here, in the intermediate region, where the danger was comparatively small under the original conditions, there has still been a considerable improvement, the average value of 0.28 volt being so small as not to involve any considerable danger to the pipes.

In group C we find that eight points which were originally negative have become more or less positive. This is to be expected in general because of the tendency to form positive areas in the region near the points where the negative feeders are tied to the

track. At these eight points there existed originally a mean value of potential difference of −0.31 volt, whereas under the insulated feeder system this has been converted into a mean value of +0.56 volt. In the more remote districts the potential differences were negative under both insulated and uninsulated systems, and are therefore of no consequence here.

These data show that under the insulated feeder system the reduction of danger is greatest at those points where there is greatest need for improvement, and the foregoing figures indicate very clearly that in the present instance the potential differences have been reduced to so low a value as to make the pipes comparatively safe. They also show that although the installation of a negative feeder system does tend to increase the area of the positive zone the positive potentials are so low as to lead to no serious consequences. One of the principal objections to the installation of insulated negative feeders that has been urged by some engineers has been that it creates a large number of positive areas covering a much greater territory than is the case with the ordinary uninsulated system. Although it is true that there is a tendency for the insulated feeder system to extend the positive area, and this is clearly indicated by the foregoing data, these data nevertheless show that comparatively few new positive points have been created, and that where they have appeared, the potential differences are so low as not to give rise to any serious corrosion of the pipes under ordinary conditions. The figures show conclusively that this objection to the insulated negative feeder system is not valid, at least in the present case, whereas the reduction of the potential differences in the regions where the conditions were originally bad is so great as to completely overshadow the effects of the slight tendency to broaden the positive zone.

All of the foregoing potential difference measurements were taken between water pipes and rails because of the greater convenience of making such measurements, since measurements could be taken between fire hydrants and tracks. In order to determine whether or not the potential differences between gas pipes and the tracks differed materially from the corresponding

voltages between water pipes and rails, a considerable number of measurements were taken between water and gas mains at accessible places. These measurements are shown in Table 7. These figures show that potential differences between water and gas mains are in nearly all cases very low, the maximum observed anywhere being 0.56 volt average for the 24-hour period, and the great majority being much smaller than that figure, the mean of all the measurements taken being 0.147 volts average for 24 hours. These figures show that potential differences between the gas pipes and rails are not much different from the values observed and recorded above for the water pipes.

TABLE 7

Potential Differences Between Water and Gas Pipes [2]

Location	Uninsulated feeders, average volts	Location	Uninsulated feeders, average volts
Eighteenth and Geyer	0.00	Selena and Victor	0.21
Eighteenth and Allen	0.05	Gravois and Shenandoah	−0.12
Eighteenth and Russell	0.05	Gravois and Victor	0.22
Eighteenth and Shenandoah	0.27	McNair and Geyer	0.02
Eighteenth and Victor	0.17	McNair and Allen	0.04
Lemp and Shenandoah	0.02	McNair and Russell	−0.09
Lemp and Victor	0.16	McNair and Ann	0.06
Mississippi and Geyer	0.09	Missouri and Ann	0.07
Mississippi and Allen	0.16	Average	0.147
Mississippi and Russell	0.44		
Mississippi and Gravois	0.56		

[2] Water pipes taken as positive

5. OVER-ALL POTENTIALS

Still another important factor in determining the probability of current being taken up by the pipes is the maximum potential differences occurring between the tracks near the station and remote points in the track network. Accordingly, a considerable number of measurements of over-all potentials were taken under both the insulated and the uninsulated feeder systems. These data are shown in Table 8.

TABLE 8

Over-All Potentials

[Voltages referred to tracks at Mississippi and Ann Avenues]

Location of outlying contact	Distance, thousand feet	Uninsulated feeders		Insulated feeders	
		Total volts	Volts per 1000 feet	Total volts	Volts per 1000 feet
Broadway and Chouteau	8.7	11.5	1.3	2.7	0.31
Broadway and Park	6.9	11.0	1.6	3.0	0.44
Broadway and Victor	5.0	11.3	2.3	0.3	0.06
Broadway and Arsenal	7.6	11.1	1.5	0.2	0.03
Ninth and Park	6.1	10.1	1.7	1.6	0.26
Ninth and Victor	4.1	10.2	2.5	−0.2	−0.05
Ninth and Pestalozzi	5.8	10.1	1.7	0.1	0.02
Twelfth and Chouteau	6.3	11.3	1.8	3.3	0.52
Twelfth and Park	4.8	9.3	1.9	2.6	0.54
Twelfth and Sidney	3.2	6.3	2.0	−0.1	−0.03
Eighteenth and Chouteau	5.4	11.3	2.1	2.7	0.50
Eighteenth and Park	4.2	8.3	2.0	2.6	0.62
Lemp and Arsenal	3.8	6.9	1.8	0.7	0.18
Jefferson and Park	5.4	11.3	2.1	2.8	0.52
Jefferson and Geyer	3.2	11.0	3.4	0.8	0.25
Jefferson and Arsenal	4.4	7.1	1.6	−1.1	−0.25
Jefferson and Cherokee	6.4	10.2	1.6	0.0	0.00
California and Chouteau	7.9	10.7	1.4	3.6	0.46
California and Shenandoah	3.4	10.0	2.9	1.2	0.35
California and Gravois	4.0	10.3	2.6	0.8	0.20
Compton and Arsenal	6.2	13.5	2.2	3.6	0.58
Grand and Arsenal	8.1	15.3	1.9	5.1	0.63
Averages		10.4	2.0	1.8	0.31

In this table column 1 gives the location of the outlying point. Column 2 gives the distance of the outlying points in thousands of feet from the point on the tracks near the station, this distance being measured along the streets by the shortest route. Column 3 gives the average potential difference between the two points. Column 4 is the total over-all potential of column 3 divided by the distance shown in column 2, and is therefore the average potential gradient in volts per thousand feet. A comparison of the potential differences and the volts per thousand feet under the uninsulated feeder system with the corresponding figures for the insulated feeder system shows the uniformly great reductions in the latter case.

An examination shows that the average over-all potential differences under the uninsulated feeder system is 10.4 volts, whereas the average over-all potential difference under the insulated feeder system is but 1.8 volts, a reduction in the ratio of approximately 6 to 1. The average gradient under the uninsulated system is 2.0 volts per 1000 feet, while under the insulated feeder system it is but 0.31 volt per 1000 feet, showing an average ratio of reduction of almost 7 to 1. These figures are in accord with all of the other data presented above, and they confirm the conclusion that a very marked improvement has accompanied the conversion of the system from uninsulated to insulated feeders.

6. SIGNIFICANCE OF TEST DATA

An examination of the preceding data on current flow in the pipes, potential differences between pipes and rails, and over-all potential differences shows that under the insulated negative feeder system these values range from one-half to one-seventh of the corresponding values which prevail under the uninsulated feeder system. These ratios represent approximately the difference in electrolysis damage that would result in the two cases.

Under ordinary conditions as they were found to exist under the uninsulated feeder system, it is probable that serious trouble from electrolysis would not have become manifest in this new district for perhaps 5 or 10 years, and if the rate of electrolytic corrosion is reduced under the insulated feeders to an average of, say, one-fifth of the original rate as indicated by the figures, the length of time that would elapse before trouble would begin to be serious would be of the order of twenty-five to fifty years. This period is so long that, for the most part, the pipes would require replacement for reasons other than electrolytic corrosion, and if such were the case the life of the pipes would not be shortened to any appreciable extent by electrolysis damage; so that the conditions shown by these tests seem to indicate that under the insulated feeder system the danger has been reduced to almost a negligible quantity.

This statement, however, should be accepted with some caution, because our investigations show that the numerical value of the potential difference between pipes and rails is not an altogether reliable measure of the rate at which damage progresses because of

variations in soil conditions. The figures are nevertheless instructive when considered as applying to average conditions, with the understanding that in special cases (and possibly in the present case) soil conditions may be such that even with the low potential differences which prevail here appreciable corrosion may still result, although the rate at which damage progresses will be but a small fraction of what it would be if uninsulated feeders were used.

The all-important conclusion to be drawn from the foregoing tests is that, regardless of what local conditions may be as regards soil conditions, the rate of damage under the insulated feeder system will be reduced to a fraction of what it would be with substantially the same amount of copper used as uninsulated feeders in parallel with the tracks.

In case experience should show that an appreciable amount of electrolysis still occurred under the insulated feeder system as now installed, we would not recommend pipe drainage in the present instance to take care of this residual trouble, primarily because of the large number of insulating joints in the gas mains. We think it would be much more effective to take care of any residual trouble that may exist by some slight extensions of the insulated negative feeder system. As for lead-covered cables, it is probable that a certain amount of drainage will always be necessary for their adequate protection, but a much smaller amount of current will need to be drawn from them under the insulated feeder system than under an uninsulated system.

7. DISCUSSION OF COSTS

COMPARISON OF COSTS OF INSULATED AND UNINSULATED FEEDER SYSTEMS AS ACTUALLY INSTALLED

The foregoing experimental data give a comparison between the insulated and uninsulated negative feeder systems on the basis of approximately the same amount and distribution of copper in each case. In dealing with the question of electrolysis mitigation, however, it is necessary to consider not only the protection secured, but also the cost of securing such protection. In Table 9 we give a detailed statement of the amount of copper in each of the insulated negative feeders as now installed, together with their

location, whether overhead or underground, and the estimated cost of installation. In calculating this cost we have assumed that the cost of installing overhead feeders is uniformly $750 per 1000 feet of 1 000 000 circular mil cable, including the cost of copper and of installation charges. For underground construction the figure of $1400 per 1000 feet of 1 000 000 circular mil cable has been used. These figures will, of course, vary somewhat, according to conditions, but they represent fair average values.

TABLE 9

Approximate Cost of Insulated Feeders, Ann Avenue Substation

Location of feeder terminal	Length, feet	Size in million circular mils	Character	Total cost installed
Lafayette and Grattan	3600	1	Overhead	$2,700
Mississippi and Geyer	1300	1	do	975
Gravois and Jefferson	2300	1	do	1,725
Gravois and California	3900	1	do	2,925
Ann and Broadway	3800	2	Underground	10,640
Ann and Ninth	2900	1	do	4,060
Ann and Twelfth	1450	1	do	2,030
Ann and Eighteenth	760	0.42	do	447
Total				25 502

Rated capacity of station, 4000 kilowatts: cost per kilowatt, $6.38.

It will be seen from an examination of Table 9 that the total cost of the negative feeders installed for this station is $25 502; the rated capacity of the station is 4000 kilowatts, giving a cost of $6.38 per kilowatt of rated capacity as the cost of the negative feeder system. Based on the same unit costs, however, we found that the cost of the original uninsulated feeder system amounted to $22 355, so that the extra cost properly chargeable against the insulated feeder system in this case is the difference between these, or $3147. In addition to the cost of copper we must also consider the value of the energy lost in the negative return.

On an examination of the data given above on the over-all potential measurements in the negative return, we find that under the uninsulated negative feeder system the mean voltage drop on the negative side was 12.2 volts, including the drop on the connections between bus-bar and tracks at the station, while under the

insulated negative feeder system, with the present amount of copper, this negative drop is increased to 19.5 volts. The net increase in negative drop has therefore been 7.3 volts. The 24-hour average current for this station is 3500 amperes, and multiplying this by the increase in voltage drop we find a net increase of power loss on the negative return of 25.55 kilowatts. Multiplying this by 8760, the number of hours in a year, we get a total of 223 818 kilowatt hours per year, which, at 1 cent per kilowatt hour, has a value of practically $2238.

The excess cost of installing the insulated feeder system over the uninsulated system was found above to be $3147, and figuring the annual cost, including interest, depreciation, taxes, etc., at 10 per cent, this amounts to $315, which, added to the $2238 representing the value of energy losses, gives a total annual cost of $2553, which is properly chargeable against the insulated system as it now stands. It should be emphasized, however, that this increase in cost is not a necessary increase, and results only from the plan that was followed of keeping the initial investment as low as possible until the experimental tests could be made.

It should be pointed out that the amount of copper now in the feeder system is such as would give a maximum economy for a maximum station output of about 3000 kilowatts, whereas the actual maximum output of the station is about 4500 kilowatts, or 50 per cent in excess of that for maximum economy. In order to get the most economical negative return system, therefore, we should increase the cross section of the present feeders by approximately 50 per cent on the average, and this would require a total increase in installation cost of approximately 50 per cent, or $12 750, which, added to the excess cost of the present system over the uninsulated system as given above, namely, $3147, gives a total increased installation cost properly chargeable to the insulated feeder system of $15 897, and 10 per cent annual charge on this gives an annual cost on the feeder installation of $1590.

At the same time, since the cross section of the feeders has been increased about 50 per cent, the drop in the negative return will have been reduced to two-thirds of its present value of 18.9 volts, giving a negative drop of 12.6 volts, which is substantially the same as the drop under the uninsulated system. In that case

there would be no appreciable change in the energy losses; consequently the above annual charge of $1590 on the installation cost represents the actual annual cost properly chargeable against the insulated feeder system. It will thus be seen that the addition of $12 750 worth of copper to the present insulated feeder system would save $2238 per year in energy losses, or about 17.5 per cent on the investment.

It is apparent, therefore, that it would be very desirable from an economic standpoint to make this increase in negative copper. In point of fact it would probably be desirable to add even more than this amount of copper, since by so doing the saving in energy loss would, up to a certain point, almost balance the increased annual cost of the installation, and thus the total annual cost would be but slightly increased, and at the same time a large reserve capacity for future growth would be had in the negative feeder system.

COMPARISON OF COSTS OF INSULATED AND UNINSULATED FEEDER SYSTEMS FOR THE SAME VOLTAGE CONDITIONS IN BOTH CASES

It is also very instructive to make a comparison of the relative costs of the two systems based on identical voltage conditions in the track return. Under the insulated feeder system the average gradient in the tracks has been reduced to 0.46 volt per 1000 feet, and if the same condition is to prevail under the uninsulated feeder system it will be necessary to have the same current distribution in the track. Consequently, we must run feeders to the same points and take off the same number of amperes from the tracks at each point, and since the feeders will be in parallel with the tracks we must further give the feeders sufficient cross section, so that they will carry this current back to the bus-bar with an average potential gradient not exceeding 0.46 volt per 1000 feet. In order to determine the amount of copper required to produce the same conditions under an uninsulated system as we have under the insulated system, it is only necessary to determine the average current carried by each feeder under the present insulated system, and calculate the amount of copper that will be required in that feeder to carry the same current with an average gradient of 0.46 volt per 1000 feet. A calculation of this sort has been made and the data are given in Table 10.

TABLE 10

Relative Cost of Insulated and Uninsulated Feeders for the Same Voltage Conditions

Feeder	Present amount of copper (thousand feet of million circular mil cable), insulated system	Average current, amperes	Amount of copper required for average gradient of 0.46 volt per 1000 feet, uninsulated system
Lafayette between Mississippi and Grattan	1.3	120	3.66
Mississippi between Ann and Lafayette	2.3	365	19.70
Mississippi between Ann and Geyer	1.3	231	7.05
Gravois btweeen Ann and Jefferson	2.3	510	27.52
Gravois between Mississippi and California	3.9	342	31.30
Ann between Mississippi and Broadway	7.6	984	87.78
Ann between Mississippi and Ninth	2.9	465	31.68
Ann between Mississippi and Twelfth	1.45	120	4.08
Ann between Mississippi and Eighteenth	0.32	207	1.55
Ann between Mississippi and substation	.....	156	.....
Total	23.37	3500	214.32

Ratio of copper required, $\frac{\text{uninsulated system}}{\text{insulated system}} = \frac{214.32}{23.37} = 9.16$

Summing up the totals of columns 2 and 4 we find that under the insulated system we have a total of 23.37 thousand feet of million circular mil cable; whereas to give identical voltage conditions under the uninsulated feeder system we would require 214.32 thousand feet of million circular mil cable. This shows that for the same voltage conditions it would require 9.16 times as much copper for the uninsulated feeder system as is required in the present insulated system.

Since the cost of the present system is $25 500, the cost of the uninsulated system using the same unit cost would be 9.16 times as great, giving a total of $233 580, which is $208 080 in excess of the total cost of the present insulated feeder system, and figuring as before 10 per cent as the annual cost on the copper installed, we get $20 808 per year as the excess annual charge on the investment in uninsulated feeders. If such a system were installed, however, it can be shown that it would reduce the potential drop in the negative return to about 2 volts, which would be a reduction of 17 volts below that which prevails at the

present time, which corresponds to an annual saving in energy of 521 220 kilowatt hours, which is worth $5212 at 1 cent per kw. hr. Deducting this from the annual charge on the copper we get a net annual charge on the uninsulated feeder system of $15 596 in excess of the annual charge on the present system. While of course it does not follow that if the uninsulated system were to be installed that the location of the feeders would be just the same as here assumed, the assumption is nevertheless approximately true, and the estimated costs are of the correct order of magnitude, and they show the impossibility, from an economic standpoint, of securing with the uninsulated feeder system approximately the same voltage conditions as can be obtained with a system of insulated feeders.

When the advantages from both the electrolysis and economic standpoints are fully weighed it seems rather surprising that insulated feeder systems have not been more widely used in the past, and we are confident that when the advantages are fully appreciated such systems will be adopted as the standard of practice, to the practical exclusion of uninsulated feeders, except in special cases where the load is so light that neither electrolysis conditions nor economic considerations require additional conductivity over that furnished by the tracks themselves.

8. APPLICABILITY OF INSULATED FEEDER SYSTEMS TO OLD STATIONS

It may be questioned whether the foregoing conclusions apply equally well to the case of an old station in which a considerable amount of negative copper has already been installed in the form of uninsulated feeders. If this copper is overhead or in conduit, it can of course be readily converted into insulated feeders at a negligible cost, so that in such a case there is no question but that the foregoing remarks would apply. If, however, the uninsulated copper is laid underground in concrete, or in such other manner as to make it impracticable to remove it or insulate it, this copper would have to be left in the form of uninsulated feeders. If there is already in place enough of such uninsulated copper to give satisfactory conditions as regards voltage drop, of course nothing additional would be required. But if the conditions are such

that it is necessary, in order to secure adequate electrolysis protection, to still further lower the voltage drops, it will be obvious from the foregoing discussion that such lowering of the gradient can be accomplished in a much more economical manner by installing the additional copper in the form of insulated feeders instead of connecting them in parallel with the feeders already in place. The old copper already installed would then be worked at a lower current density, and consequently would be used less efficiently than before, *but no less efficiently than it would be if the same voltage conditions are realized by the addition of more uninsulated copper.*

There appears to be no question, therefore, that in all cases where it is necessary to lower the potential gradients below the values already existing, such lowering of the gradients can be accomplished more economically by putting all the additional copper in the form of insulated feeders.

9. SUMMARY

The experimental data and discussion presented in the foregoing paper appear to warrant the following conclusions:

1. For substantially the same installation cost very much better electrolysis conditions can be secured with insulated negative feeders than with uninsulated feeders.

2. When the potential differences in the track return are reduced to the low values that can readily be obtained by means of insulated negative feeders, the tying in of the pipes to the tracks has a much smaller tendency to cause heavy current flow in the pipes than if such reduction of potential differences is not realized.

3. Where good voltage conditions in the negative return are maintained, the insulated feeder system can, in most cases, be installed so as to yield far greater economies both in installation and operation costs than is possible with uninsulated feeders.

4. In the case of old stations in which there is already a large amount of negative copper installed in such a way that it is impracticable to insulate it, the insulated feeder system would still be economical in case it is desired to lower potential differences in the negative return below those at present existing. Wherever

such reduction of potential differences is contemplated the insulated feeder system will show the same marked economy over the uninsulated system as is shown in the case of new stations.

5. Negative feeders which are so laid that they can not be insulated will not be used any less efficiently if supplemented by insulated feeders than if uninsulated feeders are added, provided equally good voltage conditions in the track are maintained in both cases. The opinion that such uninsulated copper is largely wasted if supplemented by insulated feeders is, therefore, based on a misconception. Uninsulated negative feeders are always wasteful wherever good voltage conditions in the negative return are required, and any addition to such uninsulated feeders is an extension of this waste; this can be avoided by using insulated negative feeders for all extension work.

In conclusion, the writers desire to express their appreciation of the coöperation extended to them by the officials of the United Railways Co., the Laclede Gas Co., city water department, and both the Southwestern and the Kinloch Telephone companies, all of whom did everything possible to assist us in our work. In particular we wish to commend the generous attitude of the officials of the United Railways Co., who willingly incurred considerable expense in connection with the installation of the feeder system, in order that the experiments could be carried out under satisfactory conditions.

WASHINGTON, December 27, 1913.

DEPARTMENT OF COMMERCE

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S. W. STRATTON, DIRECTOR

No. 33

DETERMINATION OF CARBON IN STEEL AND IRON BY THE BARIUM CARBONATE TITRATION METHOD

BY

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Bureau of Standards

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DETERMINATION OF CARBON IN STEEL AND IRON BY THE BARIUM CARBONATE TITRATION METHOD

By J. R. Cain

The disadvantages attending the use of weighed absorption tubes as means for accurately determining carbon dioxide obtained during the combustion of steels and irons are in part as follows:

1. The elaborate precautions required to prevent change of weight of the tube due to gain or loss of moisture, necessitating complications in the purifying train before and after the furnace and the use throughout the apparatus of drying agents of the same hygroscopic power.

2. Difficulties in weighing large glass vessels caused by electrical effects in wiping, by buoyancy, and by changes in temperature between balance room and laboratory.

3. The necessity for maintaining constant conditions with respect to the atmosphere within the tube, requiring sometimes a long period of aspiration after the combustion is completed.

4. The liability to error from access of gases containing sulphur and chlorine, which may be formed during combustion of the metal or of the carbonaceous residue therefrom.

5. The difficulty of determining whether the increase in weight of the tube is due solely to carbon dioxide.

6. The time lost in waiting for absorption tubes to reach a condition of equilibrium before weighing.

Those who have used absorption tubes for work requiring a high degree of accuracy know that neglect of one or more of the precautions indicated above may easily occasion errors ranging from several tenths of a milligram to 1 or more milligrams. It is evident, too, that if the complicated purifying train used with an absorption

tube gets out of order, or if the tube itself introduces error in some of the ways enumerated, it may often be a difficult matter to locate and correct the trouble. It is not surprising, therefore, that methods dispensing with the use of weighed potash bulbs, soda-lime tubes and the like are beginning to be used extensively by steel analysts. Of such methods the weighing of the carbon dioxide in the form of barium carbonate precipitate directly or after conversion into sulphate have been much used, the sulphate method abroad,[1] and the carbonate method in this country. Thus, of 62 prominent American laboratories (representing manufacturers, consumers, and testing laboratories) 32 used the potash bulb, 24 weighed the carbon as barium carbonate, 3 titrated the excess of barium hydroxide, 2 used soda-lime tubes, and 1 weighed an absorption tube filled with barium hydroxide.[2]

It is evident, in estimating the carbon dioxide by weighing the barium carbonate precipitate, or the sulphate obtained from it, that the difficulties mentioned above as peculiar to weighed absorption tubes, except No. 4, are eliminated or minimized; access of sulphur trioxide would still tend to cause high results.[3] If, however, the barium carbonate is measured by filtering it off and titrating it against standard acid, due regard being had to proper conditions for filtration and washing, there is no likelihood of error from any of the causes enumerated. The principle of this method is described in most standard textbooks on quantitative and volumetric analysis, but there seems to have been but little application in steel analysis.

The purpose of this paper is to show the special suitability of this procedure for accurate and fairly rapid steel analysis, taking up in order the sources of error or difficulty and the means of avoiding or minimizing these, and finally giving the results obtained by a series of analyses of pure sugar and of Bureau of Standards analyzed irons and steels. Without further consideration it can be seen that the adoption of this method at once simplifies the purifying train

[1] Bauer and Deiss: Probenahme und Analyse von Eisen und Stahl, 1912, p. 121.

[2] Data communicated to the author as member of a technical committee on steel analysis.

[3] There is but little likelihood of SO_2 being produced in burning steel and iron. Any small amounts of $BaSO_3$ resulting thereby would be removed by washing (see sec. 1 on Filtration and washing), the solubility of $BaSO_3$ being approximately .002 gram per 100 cc of water at 20° (Seidell "Solubilities of Inorganic and Organic Substances," 1907).

required after the furnace. Nothing at all likely to be present in the escaping gases can affect the results if we except finely divided oxides carried over mechanically as the result of a very violent combustion. No such oxides were noticed during this work or during the analyses of many other samples by different methods. If there is any reason to suspect their presence, a simple filter made by filling a U-tube with 20-mesh quartz, previously carefully washed with hydrochloric acid and water, will remove them.

The points involving sources of error which were investigated were (1) completeness of absorption of the carbon dioxide, (2) amount of washing necessary to remove the excess of barium hydroxide, (3) solubility of barium carbonate in the wash water, and (4) exclusion of extraneous alkaline substances. In addition there was devised means for the rapid filtration and washing of the barium carbonate with exclusion of carbon dioxide from the air.

I. COMPLETENESS OF ABSORPTION

This was established by burning sugar in amounts giving approximately the weights of carbon dioxide obtained during steel analysis, comparing the percentages of carbon obtained with the theoretical. As a further check two eight-bulb Meyer tubes (shown in half size in Fig. 1) were worked in series. So long as a moderate rate of bubbling was maintained no cloudiness was ever observed in the second tube. In this connection McCoy and Tashiro[4] have shown that 1.0×10^{-7} g of CO_2 can be recognized as a turbidity. If, however, the oxygen is passed too rapidly, particularly when burning steels containing more than 1 per cent carbon, some CO_2 may reach the second tube. The proper rate of gas current to retain all the CO_2 in the first tube is easily established by the operator after a few trials.

II. AMOUNT OF WASHING NECESSARY

Barium carbonate itself reacts alkaline to phenolphthalein, consequently this indicator can not be used to show when all of the barium hydroxide has been removed. The practical question as to how much washing was necessary was decided by washing the

[4] Original communication, 8th Int. Congr. Appl. Chem., 1, p. 361, 1912.

barium carbonate obtained from the combustion of accurately weighed amounts of sugar until results agreeing with the theoretical, within a small experimental limit, were obtained. The amount of wash water thus determined was increased by 25 per cent. About 150 cc wash water was usually found sufficient. The results are summarized in the recommendations later, under the head "Filtration and washing of the barium carbonate."

III. SOLUBILITY OF BARIUM CARBONATE IN WASH WATER

The possible effect of the slight hydrolysis of the barium carbonate in causing low results by solvent action of the wash water was studied by comparing the results obtained when determining the barium carbonate from the combustion of the same weights of sugar, first by washing as above described, and then with twice and three times the amount of water recommended. The results showed that the error from hydrolysis is negligible for present purposes. (See table and footnotes 8 and 9, p. 11.) Holleman [5] found the solubility of freshly precipitated $BaCO_3$ in CO_2-free water to be 1 part $BaCO_3$ in 64 070 parts water at 8.8° and 1 part in 45 566 parts water at 24.2°, or approximately 1 part in 50 000 at the temperature of the laboratory during this work, i. e., 20° to 22°. On this basis 150 cc wash water (see preceding section) would dissolve about 0.0003 g $BaCO_3$ = 0.000018 g carbon. This would be negligible for present purposes, and the amount dissolved would be really less than this because of the repression of solubility during the first washings by the barium hydroxide still present; also it is quite possible that in the rapid passage through the filter there has not been sufficient time for the wash water to become saturated with barium carbonate. Holleman's results are in good agreement with those of Bineau.[6] Holleman called attention to the fact, also recorded by Bineau, that the presence of carbon dioxide in water appreciably raises the solubility of barium carbonate, and Holleman explains in this way the solubility of 1 part in 14 137 parts of water observed by Fresenius, who left the carbonate in contact with water exposed to the air for several days.

[5] Zs. physik. Chem., 12, p. 135, 1893.

[6] Ann. chim. phys. (3), 51, p. 290.

IV. POSSIBLE SOURCES OF EXTRANEOUS ALKALINE SUBSTANCES

These are (1) substances derived by action of water on the bottles containing the CO_2-free water mentioned later; such action should be avoided by choosing a good quality of glass bottle; Jena glass containers were found satisfactory; (2) alkali carried over mechanically from soda lime guard tubes by the air used to force out CO_2-free water; thick plugs of glass wool will remove this source of danger; (3) action of barium hydroxide on the walls of the Meyer tubes; these tubes should not give up alkaline substances to the standard acid after barium hydroxide has stood in them for one-half hour and the tubes have then been thoroughly washed with alkali-free water; (4) action of barium hydroxide on filtering material; glass wool as a filling material is absolutely excluded on this ground; quartz has been found very satisfactory (see description of filtering apparatus); amphibole asbestos for the felt was found suitable from this standpoint as well as because of its resistance to attack by N/10 hydrochloric acid.

V. FILTRATION AND WASHING OF THE BARIUM CARBONATE

This is carried out with the apparatus shown in Fig. 1. The cut is approximately half-size and is self-explanatory. S is a two-way stopcock connected to the suction pipe. The rubber tubing connected to the Meyer tube should be of best grade black rubber, and the lengths used should be chosen so as to permit of easy manipulation of the tube. The Meyer tube is connected or disconnected by the rubber stoppers which are left always attached to the rubber tubes. The carbon filter C is fitted with a perforated porcelain plate, sliding easily.

The funnel is prepared for filtrations by making a felt of asbestos on the porcelain disk, using asbestos which has been digested for several hours with strong hydrochloric acid and then washed free of acid. On top of the asbestos is placed a layer of similarly washed quartz of the height shown in the figure. A mixture of grains of various sizes (approximately 50 per cent passing a 20-

mesh and the remainder passing a 10-mesh and remaining on a 20-mesh sieve) is suitable. A mixture of quartz and asbestos works well and may be simply obtained by filling the funnel with a suspension of asbestos and delivering the quartz to the funnel from a beaker by means of a strong jet of water from the wash bottle, while maintaining a gentle suction. In this way the asbestos is properly mixed with the quartz. Proper attention to these details will be found to greatly expedite filtration. The stopper is now inserted in the funnel, the Meyer tube connected as shown, and the liquid and precipitate sucked into the funnel.

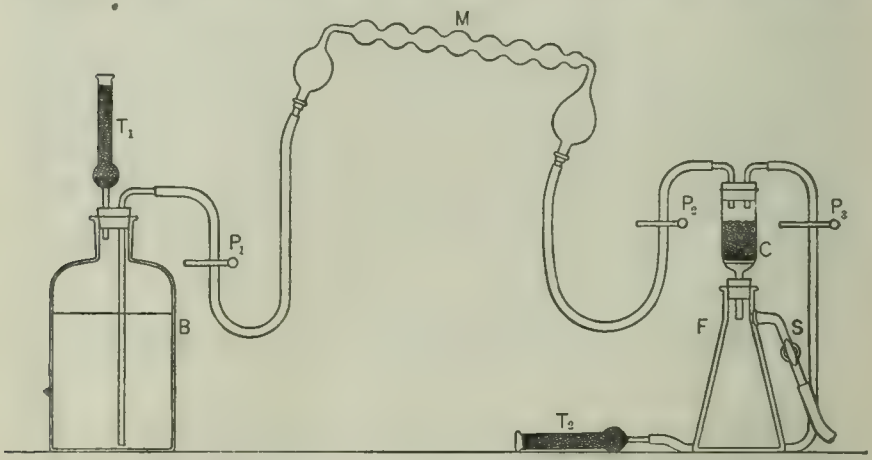

Fig. 1.—*Apparatus for filtering and washing barium carbonate*

Only very gentle suction should be used. When necessary P_3 is opened to admit air back of the column of liquid in the Meyer tube.

When the contents of the tube have all been transferred the large bulb nearest B is about half filled with water by opening P_1; the stopcock S is operated during this and subsequent operations so as to maintain a gentle suction. M is now manipulated so as to bring the wash water in contact with all parts of the interior, after which the water is sucked out through C; P_2 is left open during this and subsequent washings. After eight washings, as directed, allowing the wash water to drain off thoroughly each time before adding more, M may be detached, the stopper removed

from the funnel, and the washing completed by filling C to the top with CO_2-free water, sucking off completely and repeating the operation once. Air is now admitted through the side opening of S; C is removed and the porcelain disk carrying the quartz, asbestos, and barium carbonate is shoved, by means of a long glass rod, into the flask used for titrations, removing from the sides of C any adhering particles by a jet of water from the wash bottle.

VI. APPARATUS AND SOLUTIONS USED

1. APPARATUS

The method requires no modification of any of the accepted appliances for the combustion of iron and steel. In the present work both gas and electrically heated furnaces were used. As already stated, there was no purifying train after the furnace, the Meyer tube being directly attached. Before the furnace was an electrically heated porcelain tube filled with copper oxide, followed by a calcium chloride tower filled with stick potassium hydroxide. Steels and irons were burned on a bed of alkali and carbon free alundum contained in a platinum boat. The blanks obtained by carrying through a complete determination, including filtration, washing, etc., but with omission of any carbon-containing substance, were usually 0.0 cc and never more than 0.05 cc of N/10 hydrochloric acid, showing not only that the oxygen was sufficiently purified and the apparatus in good condition, but that the operations of filtration, washing, etc., introduced no appreciable positive error.

2. SOLUTIONS

Tenth-Normal Hydrochloric Acid.—Standardized by any of the accepted methods, or as follows: 20 cc of the approximately N/10 acid is measured out with a pipette, 5 cc of nitric acid (1 to 1 by volume) is added, and the silver chloride precipitated by an excess of silver nitrate solution in a volume of 50 to 60 cc. After digesting at 70° to 80° until the supernatant liquid is clear, the chloride is filtered off on a tared Gooch filter and washed with water con-

taining 2 cc of nitric acid per 100 cc of water until freed from silver. After drying to constant weight at 130°, the increase of weight over the original tare is noted and the strength of the hydrochloric acid calculated on the basis of the weight of silver chloride thus obtained, afterwards adjusting to the strength prescribed. Several concordant determinations with varying amounts of acid should be made. One cc N/10 HCl = 0.0006 g carbon.

Tenth-Normal Sodium Hydroxide Solution.—Standardized against the hydrochloric acid solution, with methyl orange as indicator. This solution is conveniently stored in a large glass bottle fitted with a soda-lime guard tube and arranged for delivering the solution by air pressure.

Methyl Orange.—0.02 g dissolved in 100 cc of hot water and filtered.

Barium Hydroxide Solution.—A saturated solution filtered and stored in a large reservoir from which it is delivered by air pressure, protecting from carbon dioxide by a soda-lime tube. Three or four small bulbs of the Meyer tube are filled, and CO_2-free water is added until the remaining small bulbs are filled. When burning products high in carbon the stock solution may be used undiluted.

Carbon Dioxide-Free Water.—This is conveniently made by passing air for a sufficient length of time through a soda-lime tube and into a 6 or 8 liter bottle filled with pure distilled water. The water is delivered by CO_2-free air under pressure.

VII. THE METHOD.

The combustion is carried out in the usual manner, care being taken not to pass the oxygen too rapidly. After filtering, washing, and transferring the contents of the filter to a flask, as described under "Filtration and washing of the barium carbonate," a slight excess of the standard acid is added from a burette, using a portion to rinse out the Meyer tube, and the excess of acid is then titrated against the sodium hydroxide, using methyl orange as indicator.

Results Obtained by Barium Carbonate Titration Method

Material	Weight	Carbon present	Carbon found	Difference
	g	g	g	g
Sugar [7]	0.0100	0.00421	[8] 0.00427	+0.00006
	.0100	.00421	.00420	− .00001
	.0100	.00421	.00430	+ .00010
	.0200	.00842	.00840	− .00002
	.0200	.00842	.00860	+ .00018
	.0200	.00842	.00860	+ .00018
	.0300	.01263	.01280	+ .00017
	.0300	.01263	.01280	+ .00017
	.0300	.01263	[9] .01275	+ .00012
Bessemer steel, B. S. No. 23	1.000	[10] .00805	.00805	.0000
	1.000	.00805	.00805	.0000
	1.000	.00805	.00805	.0000
	1.000	.00805	[8] .00800	− .00005
Bessemer steel, B. S. No. 10b	1.000	[10] .00373	.00372	− .00001
	1.000	.00373	.00372	− .00001
Pig iron C, B. S. No. 5b	1.000	[10] .02726	.02710	− .00016
	1.000	.02726	.02710	− .00016

Mean error, sugar	+0.000094
Mean error, steels and iron	− .000056

[7] B. S. Standard sample No. 17. A 1 per cent aqueous solution was made and the required amounts were delivered into a porcelain boat from a burette. After careful evaporation of the water the sample was burned.

[8] Washed with double the usual amount of wash water. The second portion of wash water was titrated against the N/10 hydrochloric acid; the amounts used after deducting the blank when titrating the same quantity of the water used for washing were 0.10 cc and 0.15 cc.

[9] Washed with three times the usual amount of wash water.

[10] Certificate values.

The results given in the table show that the method is as accurate as the weighing methods. It is not so subject to disturbing influences and requires less elaborate apparatus than those methods do.

VIII. NOTES AND PRECAUTIONS

1. After a little practice a precipitate can be filtered and prepared for titration in five minutes.

2. When working with steels high in carbon (above 1 per cent) it is advisable not to use more than 1 g, in order that filtration may be sufficiently rapid.

3. For very accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a determination is finished the Meyer tube should be completely filled with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

4. The flask containing the carbonate should be very thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

5. The rubber tube connecting B (see Fig. 1) to the Meyer tube should be washed with a little water from B before beginning determinations each day.

I am indebted to Mr. H. L. Cleaves, of this Bureau, who prepared the drawing of the filtering apparatus and made many determinations on steels which will appear in a later publication.

WASHINGTON, January 31, 1914.

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DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 34

DETERMINATION OF AMMONIA IN ILLUMINATING GAS

BY

J. D. EDWARDS, Laboratory Assistant

Bureau of Standards

[MARCH 2, 1914]

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1914

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DETERMINATION OF AMMONIA IN ILLUMINATING GAS

By J. D. Edwards

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I. INTRODUCTION

This paper presents the results of a brief investigation of the apparatus and methods employed for the commercial determination of ammonia in illuminating gas. It forms one of a series of technologic papers of the Bureau which present the results of investigations of methods for testing and analyzing gas. These researches are those on which are based the operating directions given in Bureau of Standards Circular No. 48, "Standard Methods of Gas Testing."

Many refinements of apparatus and manipulation were not incorporated in the work, because it was believed that the accuracy obtainable with the method recommended would be amply sufficient for the purpose for which it was desired, namely, the determination of the presence of ammonia in quantities detrimental to the usefulness of the gas, or sufficient to represent a serious loss of this valuable by-product.

The points which were investigated were the suitability of various indicators, the relative accuracy and convenience of different forms of apparatus, and the various sources of error to which the determination was subject. To have determined the absolute absorptive efficiency of the different forms of apparatus would have necessitated the preparation of a gas containing a known amount of ammonia. It was found impracticable to prepare such a gas, and so the relative efficiency, and from this the probable accuracy, was determined by running the different forms in parallel, using gas from a common supply.

II. GENERAL CONSIDERATIONS

The method generally used for the determination of ammonia in purified illuminating gas depends upon the absorption of the ammonia in a standard acid solution, the amount of ammonia absorbed from a measured volume of gas being determined either by titraton of the acid remaining unneutralized or, less frequently, by allowing the gas to pass until the change in the indicator used shows that all the acid has been neutralized.

The other constituents of the gas which dissolve in the acid affect the actual absorption of the ammonia only as diluents, but in some cases they may seriously interfere with the titration of the unneutralized acid. It is usually assumed that all basic compounds absorbed by the acid are ammonia, the traces of amines present being so small as to be of no importance. There may, however, be present in the gas constituents of an acid character whose presence must be taken into account; the most important of these is carbon dioxide. Hydrogen sulphide, and possibly hydrogen cyanide, may also interfere, but to a less extent, because they are seldom present in more than traces. These gases by

increasing the acidity of the solution might decrease the apparent amount of ammonia found in the gas, but since, in solution, they are all very weak acids the effect of their presence upon the results may be largely eliminated by titrating the excess acid with an indicator not sensitive to them. When the excess acid is titrated outside the apparatus, the interfering gases may be removed by boiling the solution under such conditions as will prevent any loss of acid, but this operation is not desirable if it can be avoided. In any case when the color change is being watched for while the apparatus is in operation, the indicator must show an end point not appreciably affected by the carbon dioxide present.

In gas-inspection work it is frequently only necessary to determine whether the ammonia content of the gas is above or below a certain limit. This can be ascertained by passing through the apparatus an amount of gas sufficient to neutralize the acid used, provided the gas contains the limiting amount of ammonia. If the color of the indicator, previously added to the acid, has then changed, it is known that the limit has been exceeded. In this manner the information desired is obtained without determining the exact quantity of ammonia present. The gas might also be passed through the apparatus until the acid is exactly neutralized, as shown by the indicator; but this, in general, is neither so accurate nor so convenient a method as that of titrating the excess acid, for the end point is hard to determine and the color change must be carefully watched for.

III. CHOICE OF INDICATORS

The choice of the proper indicator to use for this determination is of greater importance than the choice of apparatus, since the use of an unsuitable indicator may introduce large errors, amounting in extreme cases to more than 100 per cent. Many indicators have been and still are commonly used which are not at all suited to the purpose, failing to meet one or more of the following essential requirements:

1. It should show a sharp end point in dilute solutions.

2. It should be sensitive to ammonia and not be seriously affected by ammonium salts.

3. The end point should be affected as little as possible by carbon dioxide.

An investigation was made of those indicators frequently used for the determination of ammonia in gas and of some others which for theoretical reasons seemed likely to give good results.

1. EFFECT OF CARBON DIOXIDE ON TITRATION

A series of titrations (see Table 1) made under approximately the same conditions that exist in the ammonia determination shows the effect of carbon dioxide on a number of indicators. Titrations of the sulphuric acid were made with sodium hydroxide with each indicator—first, without addition of sodium carbonate; second, after addition of 4 cc of the sodium carbonate solution; and third, after addition of 20 cc of this solution. Although the addition of ammonium sulphate after completing the titration was shown to have no appreciable effect on the end point except when rosolic acid was employed (in which case the addition of 20 cc of the ammonium sulphate solution caused the end point to fade slightly), yet from 2 to 20 cc of the solution was introduced before titration in the cases indicated, to make the conditions more exactly like the conditions during a regular test on the gas. The amount of carbon dioxide probably dissolved from a gas containing 2 per cent of carbon dioxide would be about equal to that introduced by 10 cc of the N/50 sodium carbonate solution. The ammonium sulphate in 2 cc of the solution used was equivalent to that formed by the neutralization of the ammonia from 1 cubic foot of a gas containing 2 grains of ammonia per 100 cubic feet.

The sodium hydroxide solution contained a small amount of carbonate, no attempt being made to prepare a solution entirely free from carbonate. However, comparison of titrations made with and without removal of the carbon dioxide by boiling showed that the amount of carbonate present was negligible as affecting the end point with any indicator of low sensibility toward carbon dioxide.

TABLE 1

Comparison of Indicators[1]

Indicator.	H_2SO_4 (cc).	$(NH_4)_2SO_4$ (cc).	Na_2CO_3 (cc).	NaOH (cc).	Aver- age.	Apparent equiva- lent of 1 cc Na_2CO_3.	Remarks.
Methyl orange	50			44.30			Color change certain at this point; but the point could not be duplicated except by comparison. Color change very gradual.
Sodium alizarin sulphonate	50			44.95			
	50			44.91			
	50	20		44.91	44.92		End point sharp.
	50	2	4	41.14			
	50	2	4	41.17	41.16	0.94	End point good.
	50	10	20	26.30			End point somewhat indefi- nite.
	50	10	20	26.33	26.32	.93	
Cochineal	50			44.99			Addition of 10 cc $(NH_4)_2SO_4$
	50			44.96	44.98		after completing titration did not change color of end point appreciably.
	50	2	4	41.19			End point fair.
	50	2	4	41.21	41.20	.94	
	50	10	20	26.41			End point poor.
	50	10	20	26.43	26.42	.93	
Paranitrophenol	50			45.03			Addition of 20 cc $(NH_4)_2SO_4$
	50			45.16	45.10		after completing titration did not change color of end point appreciably.
	50	2	4	41.42			
	50	2	4	41.41	41.42	.92	End point fair.
	50	10	20	26.88			End point poor. Much more
	50	10	20	27.00	26.94	.91	uncertain than with sodium alizarinsulphonate under same conditions.
Methyl red	50			45.02			End point fair.
	50			45.08	45.05		Addition of 20 cc $(NH_4)_2SO_4$ after completing titration did not change end point appreciably.
	50	2	4	41.49			
	50	2	4	41.40	41.44	.90	End point fair.
	50	10	20	27.10			
	50	10	20	27.10	27.10	.90	End point poor.
Rosolic acid	50			45.96			Addition of 20 cc $(NH_4)_2SO_4$
	50			45.80	45.88		after completing titration faded end point somewhat.
	50	2	4	42.50			
	50	2	4	42.70	42.60	.82	End point very poor.
	50	10	20	31	31	.74	End point indeterminate; 31 cc is an approximation.

[1] All solutions were approximately N/50 except $(NH_4)_2SO_4$, which was N/25.

The ratio H_2SO_4 : NaOH as determined with either sodium alizarinsulphonate or methyl red in the absence of carbon dioxide was 1.113. The ratio H_2SO_4 : Na_2CO_3 under the same conditions was 1.049. From these ratios 1 cc of sodium carbonate is found to be equivalent to 0.94 cc of sodium hydroxide. The column headed "Apparent equivalent of 1 cc of Na_2CO_3" shows the magnitude of the effect of carbon dioxide. The values indicated there are obtained by subtracting the number of cubic centimeters of sodium hydroxide required to neutralize 50 cc of the sulphuric acid in the presence of the indicated amount of sodium carbonate from that required in the absence of the sodium carbonate and dividing this difference by the number of cubic centimeters of sodium carbonate added. The indicators are arranged in the table in the order of their sensibility toward carbon dioxide, methyl orange being the least affected of those tested.

As indicators relatively more sensitive to carbon dioxide are employed, the apparent alkalinity of the sodium carbonate solution decreases. In other words, the carbonic acid formed from the carbon dioxide liberated by the neutralization of the sodium carbonate gives an acid reaction with some of the indicators and must be partially neutralized by the addition of more alkali than is equivalent to the sulphuric acid before the indicator will change color. It will be noted that when using sodium alizarinsulphonate or cochineal the sodium carbonate has practically the theoretical alkali value; that is, equivalent to 0.94 cc of the sodium hydroxide. In the case of paranitrophenol and methyl red this value is slightly less, but still in fair agreement. However, when using rosolic acid the equivalent alkali value is only 0.84 when 4 cc of sodium carbonate is added and indeterminate after the addition of 20 cc.

2. CONCLUSIONS AS TO THE CHOICE OF INDICATORS

The indicators which were found to be most suitable for the determination of ammonia in gas were sodium alizarinsulphonate, cochineal, and paranitrophenol. The applicability of these, as well as other common indicators, is pointed out in the following paragraphs:

Sodium alizarinsulphonate was found to be excellently adapted for the determination of ammonia, giving uniformly good results. Its first color change is from greenish yellow to brown, and is quite sharp, even with very dilute solutions. There is a further change to rose red, but the first one should be taken as the end point. A 1 per cent aqueous solution of sodium alizarinsulphonate should be used. Two drops of the indicator solution in a volume of 100 to 150 cc will be found sufficient with this, as well as the other indicator solutions given. The end point is not affected by the ammonium salts present, and the effect of the carbon dioxide in the solution is negligible.

Cochineal changes from brownish rose to lilac. The color change is not as sharp as with sodium alizarinsulphonate, but it will give good results if properly prepared and used. The indicator solution may be prepared by grinding in a mortar 3 g of cochineal with 250 cc of 25 per cent alcohol in the cold and filtering off the undissolved residue.

Paranitrophenol gives a sharp color change, from colorless to yellow, which can be easily recognized. It is more sensitive to carbon dioxide than the first two indicators mentioned, but the results are not seriously affected unless the gas is high in carbon dioxide. A solution of 2 g in 100 cc of 95 per cent alcohol may be used.

The following indicators are either useless or unsatisfactory for the several reasons given:

Methyl orange is less sensitive to carbon dioxide than any of the above indicators, but its color changes are very gradual and the fixing of the end point is difficult, particularly with weak solutions.

Phenolphthalein can not be used because it gives an acid reaction with even small amounts of carbon dioxide in solution, and because results with it are inaccurate in the presence of ammonium salts.

Litmus can not be used, both because its end point is affected by carbon dioxide and because its color changes are too gradual and indistinct to fix the end point with the requisite degree of certainty.

Congo red is not satisfactory because its end point is not sharp enough.

Rosolic acid is too sensitive to carbon dioxide.

Methyl red has about the same degree of sensibility toward carbon dioxide as paranitrophenol, but the color change from pink to pale yellow is too indefinite.

Hematoxylin is not satisfactory because its color changes are variable and transitory. The indicator solution is not stable in the air.

IV. EFFECTS OF GLASS BEADS

The presence of the glass beads which are used in some of the absorption apparatus may lead to erroneous results for two reasons: First, the beads may yield alkali on contact with the absorbing liquid, and, second, washing of the beads may be incomplete.

1. ERRORS DUE TO SOLUBILITY OF BEADS

The amount of alkali dissolved from the beads depends upon the kind of glass from which they are made, the surface exposed, and the time they are exposed to the absorbing liquid. Although the absolute amount of alkali thus introduced is small, it may be equivalent to a considerable percentage of the total amount of ammonia to be absorbed.

The solubility of the beads can only be determined by experiment, and each operator should test the beads intended for use in the absorbing apparatus. The test may be conducted in the following manner: Wash 100 or 150 cc of the beads thoroughly with distilled water and dry them completely. Place the beads in a dry flask and add 100 cc of the acid to be used in the regular determination. Prepare a blank by placing 100 cc of the same acid in a similar flask. Stopper both flasks tightly and let stand for some convenient period, say 12 or 24 hours. Then, after thoroughly mixing, pipette out 25 cc portions from each and titrate with standard alkali. After a further interval titrate another 25 cc portion. The probable loss of acid from the beads during a determination lasting one or two hours can then be calculated. The permissible loss from this source must be determined by the operator, giving due consideration to the amount of ammonia being determined and the degree of accuracy required.

Tested in this manner the beads used in the Referees apparatus, which were of perforated cut glass 8 to 10 mm in diameter, neutralized 2 per cent of the acid in 24 hours, there being a further loss of only 0.2 per cent in the next 5 hours.

The beads used in the Emmerling, which were perforated glass beads of the usual shape, 4 to 6 mm in diameter, neutralized 1.5 per cent of the acid in 24 hours, there being no further determinable loss after 5 hours more.

A third sample, of solid spherical beads 2 to 5 mm in diameter, was also tested. These neutralized from 40 to 60 per cent of the acid in 24 hours, and there was a further considerable neutralization during the next 5 hours. Since continued soaking did not appreciably reduce their solubility, these beads were evidently unsuitable and were not used in any of the remaining experimental work.

2. ERRORS DUE TO INCOMPLETE WASHING

The washing of a large column of beads to render them free from acid is an operation which is tedious and uncertain, particularly when the volume of wash water which it is permissible to use is comparatively small. The difficulties of titrating a small amount of acid increase greatly with dilution of the acid, and so it is quite necessary that the amount of wash water should be kept as low as possible. Perforated beads especially retain traces of the acid very tenaciously and about the only certain method of removing the last traces of acid is to completely cover the beads with several portions of the wash water; merely allowing the water to run over the beads is not sufficient. In the Referees apparatus, however, the chamber occupied by the beads is quite large, and it is impracticable to fill the apparatus completely with water when washing it out. The best plan, therefore, is to use several 50 to 75 cc portions of water and allow each portion to wash the beads as much as possible by rotating the cylinder before draining.

The bead column in the Emmerling tower required only 30 cc of wash water to flood the beads, and washing could be made practically complete with less than 100 cc of water.

TABLE 2

Loss of Acid in Washing Out Apparatus Containing Beads [2]

Apparatus.	H_2SO_4 added (cc N/50).	H_2SO_4 unrecovered (cc N/50).	NH_3 equivalent of H_2SO_4 lost (grains per 100 cu. ft. calculated for 1 cu. ft. sample).
Referees apparatus	28.83	0.22	0.11
	28.45	.08	.04
	15.00	.27	.14
	15.06	.20	.10
Emmerling tower	15.47	.07	.04
	15.02	.03	.02

[2] Sodium alizarinsulphonate used as indicator. Three 75 cc portions of wash water used in Referees; two 30-cc portions used in Emmerling.

Table 2 shows the losses which occurred in several experiments in washing out both the Referees apparatus and the Emmerling tower. The acid was placed in the apparatus, allowed to come in contact with all the beads, and then washed out just as in the regular determination. The time in the apparatus was less than 10 minutes, so that the results are not affected by the solubility of the beads. The last portion of wash water used gave a neutral reaction with the indicator. It will be observed that practically all of the acid is recovered from the Emmerling tower; but the losses in the Referees apparatus are somewhat variable, being appreciable, but nevertheless small enough to be negligible in any ordinary work.

To insure completeness of washing, the operator should test his procedure by placing in the apparatus the amount of acid used in a determination and washing with successive portions of wash water until a portion is secured which is neutral to the indicator used. If the amount of wash water thus shown to be necessary is excessive, the volume of each portion should be reduced and the number increased as may be necessary.

V. TESTS OF APPARATUS

1. DESCRIPTION OF APPARATUS

Various forms of gas wash bottles have been used for absorbing the ammonia, but a few special types have best met the conditions of service and come into practical use. The following five forms have been considered in this paper.

(a) **Referees Apparatus.**—The Referees apparatus is the well-known form, first used by the London Gas Referees. It consists of a glass cylinder filled with beads and having stopcocks at one or both ends. Some dealers are supplying this apparatus with metal cocks or connections cemented to the glass ends; but both the cement and the metal are quickly attacked by the acid and make results obtained by the use of such apparatus unreliable. The form figured is that used in these tests. It was necessary to have

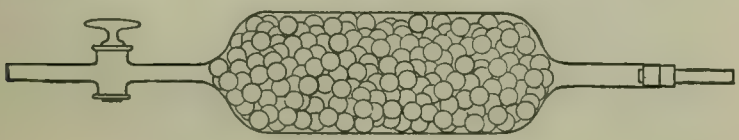

Fig. 1.—*Referees apparatus (¼ size)*

a stopcock at one end so that the apparatus could conveniently be held vertically when filling with acid, but the tube at the other end, which was used as the outlet, was made without stopcock and larger, so that acid and wash water could be easily introduced. In this outlet was placed a perforated rubber stopper carrying a glass tube.

(b) **Emmerling Tower.**—Although the Emmerling tower is also filled with beads, it is essentially different from the Referees form in operation, for the gas is required to bubble through the acid, while in the Referees apparatus it only passes over the surface of the acid. Emmerling towers are made in many different sizes and proportions, the one used (Fig. 2) being of 2.2 cm internal diameter and holding conveniently a bead column 10 cm in length, which was found to give satisfactory results. The usual form is illustrated, but it could be better adapted for this particular purpose by plac-

ing the outlet tube on the same side as the inlet, or by using a glass tube in the rubber stopper as the outlet. Then there would be no danger of losing acid through the outlet if the apparatus was inclined too near to the horizontal.

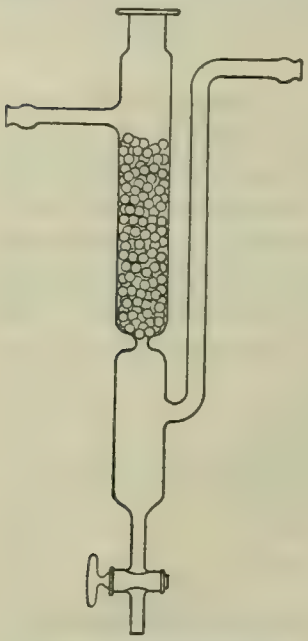

Fig. 2.—Emmerling tower (¼ size)

Fig. 3.—Hinman apparatus (¼ size)

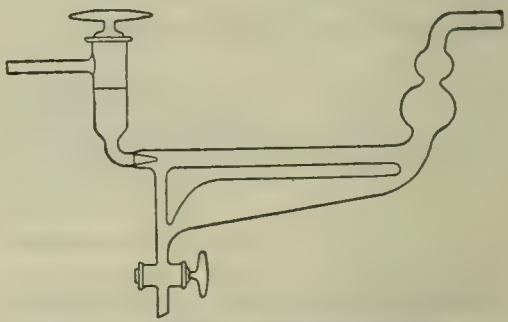

Fig. 4.—Modifted Cumming wash bottle (¼size)

(c) **Hinman Apparatus.**—This apparatus was primarily designed for traveling inspection work, and being small and light it is readily portable; the form and construction is apparent from Fig. 3.

(d) **Modification of Cumming Wash Bottle.**[3]—This apparatus was designed at the Bureau of Standards for this work. (See Fig. 4.) The object in view was to obtain a gas wash bottle which would operate under low pressure and yet give complete absorption and

[3] Chem. News, 101, 39; 1910.

continuous circulation of the acid. Furthermore, it was so constructed that it may be permanently connected, as when used in series with the sulphur apparatus, and be filled and washed out without changing any of the connections. The gas passing through the small nozzle acts like an injector and circulates the liquid rapidly and continuously, thus bringing fresh acid into contact with the gas. Any color change of the indicator can therefore be easily determined, for the liquid is very nearly of constant composition throughout the apparatus.

(e) **Wash Bottle.**—The common gas wash bottle was tested because its availability is a strong point in its favor when it is to be used in gas-inspection work where the other forms might not

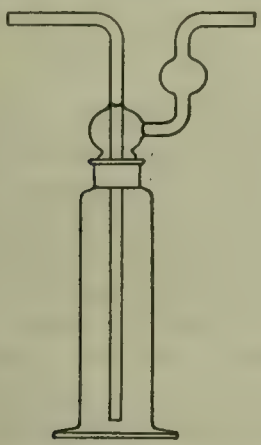

Fig. 5.—*Wash bottle (¼ size)*

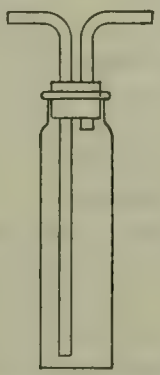

Fig. 6.—*Wash bottle (¼ size)*

be obtainable. The form used (Fig. 5) was of glass with a ground glass joint at the top, but one just as efficient can be easily made from a tall glass bottle, closed with a rubber stopper bearing an inlet and an outlet tube as shown in Fig. 6. The depth of liquid in the bottle as well as the size and shape of the bottle will affect the absorption, but the depth of liquid is limited by the gas pressure available for its operation. In the following experiments the bottle used had an internal diameter of 4 cm, was 18 cm high, and the gas bubbled through 4 to 6 cm of solution.

2. COMPARISON OF APPARATUS

(a) **Meter Comparison.**—For comparison, four different forms of apparatus were run at the same time from a common gas supply under as nearly uniform conditions as possible. The gas meters employed were all of the wet type. Since only comparative results were desired, the meters were not calibrated, but compared with one another by running them in series. This comparison was repeated at intervals throughout the work and the agreement found to be satisfactory, no change taking place large enough to have any appreciable effect upon the results. When only 1 or 2 cubic feet are used in a determination, the error incident to taking fractional parts of a revolution of the meter may be appreciable; it might amount to 1 per cent of the volume of the gas if only 0.5 cubic foot is used. The effect of this error would, of course, be reduced by using a larger amount of gas.

(b) **Gas Supply.**—The regular city gas supplied to the Bureau was used, but in a large number of the runs ammonia was added to it, since its normal content is only about 1 grain per 100 cubic feet.[4] The ammonia was introduced into the gas by means of the following apparatus: A 30-liter bottle was fitted with a rubber stopper bearing two inlets and a stirring apparatus. This latter, consisting of a small fan inserted through the stopper and operated by a small electric motor, served to mix thoroughly the contents of the bottle. The gas was introduced through one inlet and a smaller amount of gas, which had passed through a tube containing several lumps of ammonium carbonate, through the other. This latter gas bubbled through a small wash bottle before passing through the ammonium carbonate tube, so that the amount of ammonia being introduced could be gauged approximately by the number of bubbles of gas passing per minute. The gas, after being mixed in the first bottle, passed through an outlet near the bottom into a similar bottle through a narrow glass tube reaching two-thirds of the way to the bottom. The gas

[4] Although it is the universal practice in this country to express the results in grains ammonia per 100 cubic feet of gas, these figures convey no adequate impression of the volume relation of the ammonia to the other constituents of the gas. One grain of ammonia per 100 cubic feet, measured at 30 inches and 60° F (762 mm and 15.55° C), is equivalent to 31.6 parts of ammonia per million by volume.

used was withdrawn from the top of this second bottle and distributed through a system of T-connectors, delivering the same quality of gas to each apparatus. All connections were made as far as possible by means of glass tubing held together by short pieces of heavy walled rubber tubing.

(c) **Absorbing Liquid.**—An approximately N/50 solution of sulphuric acid, standardized by precipitation with barium chloride, was used as the absorbing agent.

For titrating the excess acid a solution of sodium hydroxide of approximately equivalent strength was used, the exact ratio between it and the acid being obtained by titration in the same volume of solution as during an actual determination.

It was not considered desirable to use a stronger solution of acid because of the small amount of ammonia to be absorbed and the fact that small errors in the measurement of stronger solutions make a large error in the ammonia apparently absorbed. Should it be desirable to extend the operation over long periods of from 10 to 20 hours, in order to obtain an average for that period, it may be necessary to use a stronger acid solution. The amount of ammonia likely to be absorbed is the factor which should determine the strength of acid to be used. Other conditions being equal, the greatest accuracy is obtained when the major part of the acid in the apparatus is neutralized by the ammonia in the gas.

(d) **Operation of Apparatus.**—About 25 cc of the standard acid was placed in each of the different forms of apparatus, except the Hinman, which required only about 15 cc; then a small amount of water was added, to bring the solution in each up to the volume required for its most efficient operation. Connection was then made between the gas mixing bottle and the apparatus, and a meter was connected to the outlet of each apparatus. All four forms were started at the same time and the flow of gas to each was carefully adjusted to the desired rate. Although the rate fluctuated somewhat, owing to changes in the gas pressure, no governor being used, it was maintained as nearly uniform as possible by close observation and regulation. The rate given in the table is the average rate for the whole run.

TABLE 3

Comparison of Ammonia Absorption Apparatus [5]

Test number.	Time of run, min.	Average NH_3, grains per 100 cu. ft.	Hinman.			Modified Cumming.			Wash bottle.			Referees.			Emmerling.		
			Rate, cu. ft. per hr.	NH_3, grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH_3, grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH_3, grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH_3, grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH_3, grains per 100 cu. ft.	Variation from average, per cent.
1	60	20.50	0.5	19.48	−5.0	0.5	20.91	+2.0				0.5	20.36	−0.7	0.5	21.24	+3.6
2	85	12.25	.54	12.42	+1.4	.56	12.34	+0.7				.50	11.98	−2.2	.54	12.26	0.0
3	70	11.68	.6	11.81	+1.1	.6	11.74	+0.5	0.63	11.52	−1.4				.65	11.65	−0.3
4	100	6.81	.65	6.78	−0.4	5	6.74	−1.0				.5	6.82	+0.1	.5	6.90	+1.3
5	90	6.42	.61	6.46	+0.6	62	6.44	+0.3	.57	6.31	−1.7				.60	6.46	+0.6
6	120	5.33	.78	5.45	+2.2	.57	5.26	−1.3	.64	5.23	−1.9				.68	5.38	+0.9
7	120	3.85	.77	3.77	−2.1	.66	3.77	−2.1	.72	3.72	−3.4				.73	4.13	+7.3
8	120	3.66	.53	3.67	+0.3	.53	3.55	−3.0				.56	3.77	+3.0	.51	3.66	0.0
9	60	2.69	.60	2.79	+3.7	.60	2.72	+1.1	.61	2.60	−3.3				.60	2.65	−1.5
10	270	.80	.63	.79	−1.3	.62	.80	0.0	.59	.77	−3.8				.64	.83	+3.8
11	60	6.38	1.10	6.34	−0.6				.98	6.38	0.0	1.03	6.40	+0.3	1.05	6.38	0.0
12	60	3.99	1.00	3.90	−2.3				.98	3.90	−2.2	1.01	4.14	+3.8	.97	4.00	+0.2
13	105	.95	1.00	.92	−3.1							1.01	1.01	+6.3	1.01	.93	−2.1
Average, 1 to 10					+0.5			−0.3			−2.6			+0.05			+1.6

[5] Sodium alizarinsulphonate used as indicator.

(e) **Results of Comparison.**—Table 3 shows the results of 13 runs with gas of varying ammonia content. The data for each run are arranged in a single line, designated at the left by the number of the test. All results secured are recorded with the exception of two runs where irregularities of operation interfered and made the results valueless, despite the fact that fair agreement was secured. The value recorded in column three, "Average NH_3, grains per 100 cu. ft.," is obtained by averaging the four results obtained with the different apparatus. The values in the column headed "Variation from average" are the differences between the average and the value secured with that particular apparatus expressed as a percentage of the average. While the average value may be no nearer the correct value than any of the four individual results, it affords a convenient means of comparison and the results indicate the general tendency of the different forms of apparatus. The average variation from the mean as shown at the foot of the table is only for tests 1 to 10, since the last three were made at a much higher rate and, therefore, are not comparable on the same basis as the others. Two different Referees apparatus were used, identical in shape, but one slightly smaller than the other. Tests 4, 11, 12, and 13 were made with the smaller apparatus. Sodium alizarinsulphonate was used as the indicator, and the excess acid titrated in every case except with the Hinman apparatus in tests 1 and 2, where gas was passed through the apparatus until the change of color of the indicator indicated saturation of the acid by the ammonia.

It is seen from a consideration of these results that those obtained with the Emmerling tower are somewhat higher than those obtained with the other forms, and that the wash bottle gives results consistently lower. The other three ran about the same.

In order to determine whether any appreciable amounts of ammonia escaped unabsorbed, a second series of tests (Table 4) was made. In these tests the gas after leaving the first absorption apparatus passed through an Emmerling tower, the acid in which was then titrated as usual. Since the gas receives a very thorough washing in its passage through this apparatus, it is reasonably certain that any ammonia escaping absorption in the Emmerling

tower thus used must be a very small percentage of the total and in any case entirely without interest as affecting the quality of the gas. As seen in Table 4, in all but two of the experiments the amount of ammonia thus absorbed in the Emmerling tower was not detectable within the limits of error of the titration.

TABLE 4

Tests of Completeness of Absorption [6]

First absorption apparatus in series with Emmerling.	Rate of passage of gas, cu. ft. per hour.	NH_3, grains per 100 cu. ft.	NH_3 in Emmerling, grains per 100 cu. ft.	Percentage of NH_3 absorbed in second bottle.
Hinman	0.62	9.64	0.0	0
	.66	21.65	.2	1
Referees	.60	25.60	.0	0
	.66	8.50	.0	0
Modified Cumming	.52	15.20	.0	0
	.57	5.34	.0	0
Wash bottle	.61	4.26	.0	0
	.57	4.53	.1	2

[6] Titrations made with sodium alizarinsulphonate as indicator.

3. CONCLUSIONS AND RECOMMENDATIONS REGARDING APPARATUS

The accuracy obtained in practice will, of course, depend upon the accuracy with which the gas is measured, the certainty with which the ammonia equivalent of the acid is known, and the completeness of absorption of the ammonia. With careful operation, any one of the five forms of apparatus tested would ordinarily give results that are well within the limits of accuracy required for this determination, either for commerical control work or for the purpose of gas inspection.[7] The wash bottle appears to be slightly less efficient as an absorber than the other forms, but still it gives satisfactory results. Any increase in the accuracy which might be secured by a more complete absorption train and the removal of interfering gases would not generally be practicable because of the increase in time and labor involved.

[7] It is difficult to make any comprehensive statement defining satisfactory results. In general, results on gas containing up to about 5 grains of ammonia per 100 cubic feet should be within 10 per cent of the ammonia content of the gas, although the percentage error may be greater when the ammonia is 1 grain or lower. With gas containing more than 5 grains ammonia, the percentage error should decrease somewhat. The interpretation of results is discussed in Bureau of Standards Circular No. 48.

Referees apparatus.—Balancing the possible loss of acid due to neutralization by alkali from the beads or by retention of acid after washing is the possibility of ammonia escaping from the Referees apparatus; a danger somewhat greater than with other forms because the gas passes over only the wet surface of beads and cylinder and may quickly saturate the acid exposed without neutralizing the main bulk of liquid in the bottom of the apparatus. It was frequently observed, when an indicator had been added to the acid, that the beads along the top had changed color because of saturation by the ammonia of the liquid adhering to them and that this color change sometimes extended to the outlet, the bulk of the liquid being still unaffected. Owing to the solubility of the ammonia in water there may be no loss even after the surface liquid has become saturated, but it is believed that ammonia sometimes escapes this way. The cylinder should be rotated from time to time to moisten the top beads with fresh acid. The cylinder should also be completely filled with beads, so that there is small opportunity for the gas to follow channels and so escape thorough washing. At higher rates, up to 1 cubic foot, the Referees apparatus gives better absorption than either the Hinman or the modified Cumming. The Referees apparatus, as noted in a previous paragraph, should be made without metal parts, and the outlet is best closed with a rubber stopper carrying a glass tube. As this apparatus is clumsy to handle it is not recommended for traveling work. However, it operates with very small difference of pressure between inlet and outlet, which is frequently a great advantage, particularly when being used in series with a sulphur apparatus.

Emmerling tower.—The Emmerling tower seems to give somewhat better absorption than the other forms. Since only a small column of beads is used, it can be easily washed by bubbling a little air through to agitate the wash water covering the beads. The same attention should be paid to the resistance to solution of the beads used as with the Referees apparatus. The principal objection to the Emmerling form is the fact that it requires a larger pressure to operate than some of the other forms. The pressure necessary depends, of course, on the amount of liquid in the appa-

ratus and the angle at which it is inclined. In addition to its efficiency as an absorber, another point in its favor is the fact that it can be filled and emptied without breaking the connections. It may be used at higher rates, say 1 cubic foot per hour, with safety.

Hinman apparatus.—The Hinman is a satisfactory form to use; it is light and easily portable, being especially adapted for traveling inspection work. The circulation of acid is often poor, and when a test is being run to determine whether saturation of the acid has taken place it is necessary to mix the contents of the bulbs thoroughly before a reliable observation can be made. The Hinman should be so filled and set that the gas is required to bubble past each of the constrictions. Care should be taken that loss of acid does not occur by bubbles breaking too close to the outlet. The gas should be passed at about 0.6 cubic foot per hour.

Modified Cumming apparatus.—This apparatus gives good absorption when run at rate of 0.6 cubic foot per hour or less. The circulation of the liquid is excellent and any change of color can be easily observed. The pressure required to operate it is low. It can be permanently connected, being emptied and filled without changing the connections, which makes it very convenient to use in a permanent set up in series with a sulphur apparatus.

Wash bottle.—The wash bottle is evidently not quite as efficient an absorber as the other forms. Where an accuracy of 10 per cent is sufficient the wash bottle may be found useful because of its availability. The bottle should be tall and narrow, the amount of acid being used depending on the pressure available for its operation. Two bottles in series may be used where greater accuracy is desired. They will require greater pressure to operate, which may prevent their use where the pressure is low. Gas should be passed at a rate not greater than 0.5 to 0.6 cubic foot per hour.

VI. SUMMARY AND RECOMMENDATIONS

Four common forms of apparatus for the determination of ammonia in gas, and a new form designed on the principle of the Cumming wash bottle were tested. The results show that the amount of ammonia in a gas can be determined with sufficient

accuracy for official or commercial testing with any of the five forms. The advantages and disadvantages of each form as well as precautions to be observed in operation are pointed out in the text.

It is recommended that the ammonia be determined by absorption in sulphuric acid with subsequent titration of the excess acid and not by passing gas through the apparatus until a color change is shown by the indicator. It is satisfactory, however, when it is only desired to know whether the ammonia content is above or below a certain limit, to pass a predetermined volume of gas and note whether the acid has been completely neutralized or not.

Sodium alizarinsulphonate, cochineal, and paranitrophenol have been found to be satisfactory indicators.

The use of a N/50 solution of sulphuric acid as an absorbing agent is recommended, although the strength may be varied to meet different conditions.

The errors due to incomplete washing and the use of glass beads are discussed, and means of eliminating their effect are given.

Full directions for carrying out the determination, preparation of standard solutions, calibration and use of meters, etc., will be found in Bureau of Standards Circular No. 48, "Standard methods of gas testing."

To Mr. R. S. McBride are due the author's thanks for the continued help and advice given during the course of this work. Preliminary experiments on this determination were made by Mr. E. R. Weaver, and the author wishes to express also his appreciation of the assistance gained from Mr. Weaver and his experience.

WASHINGTON, March 2, 1914.

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No. 35

COMBUSTION METHOD FOR THE DIRECT DETERMINATION OF RUBBER

BY

L. G. WESSON, Laboratory Assistant

Bureau of Standards

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COMBUSTION METHOD FOR THE DIRECT DETERMINATION OF RUBBER

By L. G. Wesson

The method most in use at the present time for the determination of the caoutchouc content of rubber goods is an indirect one, in which the sample is analyzed for its moisture, mineral matter, sulphur, resin, and other contents, these values being then added together and the sum subtracted from 100 per cent to arrive at the percentage of rubber present. As many of the best methods for estimating these constituents are admittedly inaccurate, the indirect method is not a satisfactory one. A number of direct methods have been proposed and thoroughly tested, but as they depend for their accuracy on certain derivatives of rubber, the nitrosite, the nitrosate, and the tetrabromide, that have not thus far been obtained with unvarying composition, these methods have not found general acceptance either as technical or research methods for this extremely important estimation. It is hoped that the method [1] about to be described will lend itself to development not only as a dependable one for rubber research work, but also for the commercial laboratory.

The procedure, in brief, consists first in forming the nitrosite of rubber by the action of nitrogen trioxide gas upon a finely ground and acetone-extracted sample of the rubber suspended in chloroform. After the completion of the action, the insoluble nitrosite, fillers, etc., are filtered from the chloroform, and the nitrosite is dissolved in acetone. The suspension of finely divided mineral matter is then allowed to settle out, or is thrown down with the centrifuge. An aliquot portion of the solution is transferred with a pipette to a small flask, and its volume reduced by evaporation

[1] A preliminary note on this method was published in the Journal of Industrial and Engineering Chemistry, 6, p. 398, 1913.

to a few cubic centimeters. This small volume of acetone solution of the nitrosite is now transferred with the help of ethyl acetate to a porcelain boat containing alundum, and, after the acetone and ethyl acetate have been expelled by warming the boat for several hours in a drying oven, the nitrosite is burned in a current of oxygen and the carbon dioxide thus formed is absorbed in soda-lime and weighed. If all of the carbon originally in the sample as rubber, and only such carbon, reaches the soda-lime apparatus as carbon dioxide through the intermediate nitrosite, the equation $C_{10}H_{16} = 10CO_2$ enables one to calculate the $C_{10}H_{16}$ or real caoutchouc content of the sample.

PROCEDURE AND APPARATUS IN DETAIL

The procedure and apparatus employed in obtaining the results given later are the outgrowth of many trials and experiments. Doubtless deviations are allowable in many points, but there was not opportunity to study the effect of changing various factors.

The sample should be ground to pass a 20-mesh sieve if possible, or cut up fine with the scissors if very soft. A weighed amount of the sample, 0.5 g for compounds containing about 50 per cent or less of rubber and 0.25 g for those containing a higher percentage, is wrapped into a bundle with a 9-cm filter paper and extracted for three to four hours with acetone in an apparatus of the Wiley or Cottle type, in which the sample is extracted by the solvent at the boiling point of the latter. The residue, from which the excess of acetone has been squeezed with the fingers, is then transferred to a 50-cc calibrated, glass-stoppered flask and allowed to dissolve or swell up in about 40 cc of chloroform,[2] which action may be hastened by warming the flask.

The rubber is now submitted to the action of nitrogen trioxide gas, evolved by running nitric acid of specific gravity 1.3 dropwise on arsenic trioxide contained in a flask warmed in a boiling water bath. After the gases have been passed through an empty gas-washing bottle to condense most of the moisture and nitric acid carried over from the generator, they enter the chloroform through a delivery tube joined by a rubber connection to the gas-

[2] The chloroform should not be previously dried, as moisture is apparently advantageous in giving a more rapid action of the nitrogen oxides on the rubber.

washing bottle and fitting closely end for end to the same. The flask containing the chloroform should be immersed in a beaker of cold water during the reaction, since the solubility of the oxides of nitrogen in chloroform is increased and the danger of the gas exerting a partial oxidation of the rubber to CO_2 is probably diminished thereby. The gas should be passed into the chloroform until a deep green color is obtained which is permanent for at least 15 to 20 minutes after the delivery tube has been disconnected from the gas generator.

The next morning the chloroform is decanted off, using gentle suction, through a small Gooch crucible provided with a mat of dry asbestos. If the filtrate is colored brown from the dissolved gases, one can be certain that a sufficient excess of the nitrogen oxide has been used. After the flask has been rinsed out several times with small volumes (5 cc) of chloroform, each time decanting carefully through the crucible, the excess of chloroform and acid vapors which remain in the flask should be expelled by the passage for a few minutes of a gentle air current through the original delivery tube. If some nitrosite from the rubber connection is on the upper end of this tube, it may be easily removed by moistening it with acetone and wiping clean with a piece of filter paper.

The nitrosite in the crucible is then dissolved by placing the crucible in a 75-cc beaker, adding successive small portions of acetone, and pouring each into the original flask until about 40 cc has been used. No harm is done if a portion of the asbestos gets into the flask. In the meantime, the delivery tube has been freed from the nitrosite by sucking some of the acetone up into it from the beaker and rinsing the outside into the same. Let the flask now remain in a beaker of water with occasional shaking, without stoppering, for a half hour to insure complete solution of the nitrosite in the acetone. The volume is now made exactly to the mark, the flask stoppered and shaken, and to obtain a clear solution the insoluble mineral matter is allowed to settle, or better, is quickly centrifuged out; 1500 revolutions per minute is sufficient to give a clear solution in from 5 to 10 minutes.

To regain the original temperature the flask is now allowed to stand again in the beaker of water until the correct volume is once more attained. An aliquot portion of the solution (25 cc) is now

pipetted to a 50-cc Erlenmeyer flask. To reduce the bulk of this solution to a few cubic centimeters the flask is warmed in a dish of water while a current of air is blown into the flask. The acetone should not be completely expelled. The nitrosite is transferred from the Erlenmeyer flask to a porcelain boat 14 cm long by 1.1 cm wide, and about two-thirds full of alundum,[3] which is used to secure an even combustion of the nitrosite. The acetone solution of the nitrosite should not be poured into the boat, but should be drawn up into a small (2-cc) pipette and run out evenly over the alundum. Several 2 to 3 cc portions of ethyl acetate [4] are then used to rinse out the remainder of the nitrosite, using a small wash bottle and the pipette for this purpose. Ethyl acetate is used for the expulsion from the nitrosite of acetone which is otherwise retained in small amounts, perhaps mechanically by the nitrosite or by the portion of the mineral matter which passes in solution with the nitrosite into the boat, or by reaction with the nitrosite during drying. When enough wash liquid has been added to the boat to show above the alundum, the most of it should be expelled by placing the boat for a few minutes in the drying oven. The same procedure should be repeated at least once, using small portions of ethyl acetate in the transfer as described above. When one is certain that no nitrosite remains in the flask or pipette, the boat is dried for two hours at about 85° C. A circulation of air in the oven to carry away the acetone and ethyl acetate vapors will assist the drying greatly. The nitrosite is now ready for the combustion.

The combustion apparatus as it was finally developed contains features already used outside of this laboratory,[5] and others original either with my colleagues or myself. The arrangement of the parts is best understood from the figure.

The tube is of Jena combustion glass, or better, of quartz, 50 cm long and 1.5 cm bore. The nitrosite is decomposed by the heat of an external coil, made by winding two layers of nichrome

[3] "RR" alundum, 90-mesh, specially prepared for carbon determinations. Norton Co., Worcester, Mass. A fresh portion should be used for each combustion.

[4] The so-called "absolute ethyl acetate," containing about 2 per cent of alcohol. It should be redistilled before use, since it may contain other organic substances not easy to volatilize.

[5] The most important of these are the electrically heated platinum coil used as a catalyzer (Morse and Taylor, Am. Chem. J., **33**, p. 591, 1905); and the electrically heated external coil used for the decomposition of the substance to be burned.

ribbon,[6] leaving 0.1 cm between the turns, on an asbestos-covered copper or brass tube, 5 cm long and of such a diameter as to leave a 0.3-cm space between the metal and the combustion tube; and then covering it with asbestos paper to form an insulating layer 1 cm thick. During the combustion the coil as it moves forward should never be moved so fast that its forward end reaches more than 1 cm beyond the border between the black carbon of the undecomposed nitrosite and the white alundum of the completely burned portion. The decomposition products are carried forward by the current of oxygen over a red-hot spiral of platinum wire, which serves as the catalyzer for complete oxidation. The spiral is made from 1.3 m of No. 20 wire wound into a cylinder 0.7 cm in diameter, and is supported in the middle of the tube by an unglazed porcelain or clay stem 12 cm long and 0.3 cm in diameter, the return end of the spiral passing back through the stem. The leads for the spiral are 8 cm long and are made with No. 10 platinum wire. One end of the pipestem is supported by these leads and the other end by a small leg of platinum wire. The leads may connect with the outside in one of several ways. There may be a rubber stopper at the forward end of the tube through which are pushed two heavy copper, nickel, or platinum wires, the ends of which are bent into small loops into which the platinum leads are placed before the insertion of the stopper. Nickel is the better of the first two metals named. The platinum wires are good, as they may be sealed into small glass tubes which reach just through the stopper. In any case the stopper soon deteriorates, although this action has no noticeable effect on the results of the combustion. The most satisfactory method, however, consists in drawing down the forward end of the combustion tube as in the diagram, joining on a 3-cm tube of 0.5-cm bore, and sealing in two 3-cm lengths of heavy platinum wire. These are bent up on the inside and the platinum leads are thrust forward so as to rest upon them.

The oxides of nitrogen formed during the combustion of the nitrosite are absorbed by a saturated solution of potassium bichromate in concentrated sulphuric acid. Acid vapors and sulphur trioxide are held back by 30-mesh granulated zinc. Attention is

[6] 0.11×1/32″, R=1.3 to 1.5 ohms per foot. Driver Harris Wire Co., Harrison, N. J.

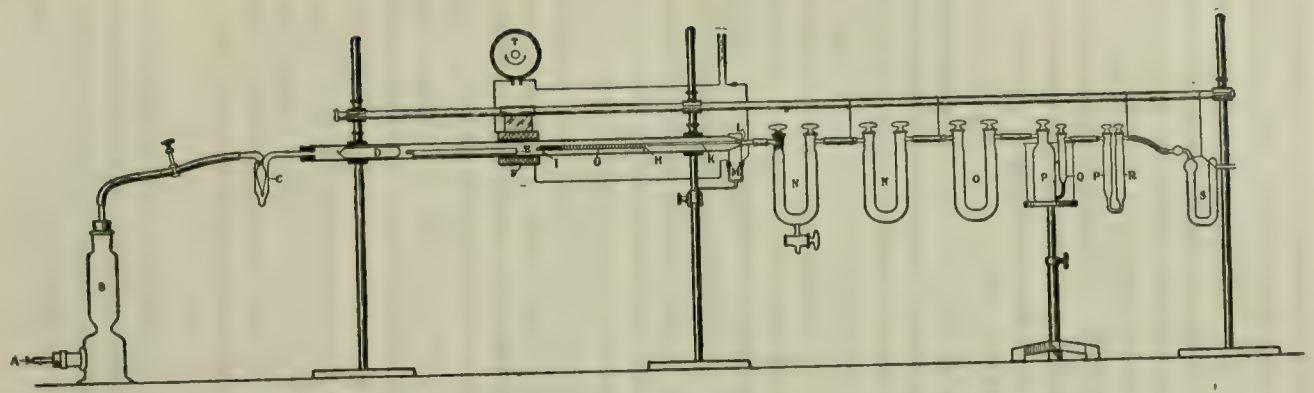

Fig. 1.—*Form of apparatus for combustion of nitrosite and absorption of carbon dioxide*

A. Oxygen enters.
B. Moist soda lime.
C. Bubble counter containing sulphuric acid (Dennstedt).
D. Closed tube of Jena combustion glass, 8 cm long, to prevent diffusion backward.
E. Porcelain boat.
F. Heating coil of nichrome ribbon.
G. Platinum spiral, about 10 cm long, of No. 20 wire.
H. Porcelain stem.
I. Platinum leg for supporting stem.
K. Platinum leads, 8 cm long, of No. 10 wire.
L. Short platinum wires sealed into tube.
M. Mercury contacts.
N, N. U tube containing glass beads and H_2SO_4–$K_2Cr_2O_7$.
O. U tube containing 30-mesh granulated zinc.
P, P. Soda lime.
Q. Calcium chloride.
R. Alumina.
S. U tube containing palladium chloride solution.
T. Rheostat.

called to the form of apparatus in the figure for the absorption of carbon dioxide by soda lime. The capillary tube makes a good substitute for a stopcock on account of its comparative lightness, and is effective in separating the moist soda lime from the calcium chloride. Empty, the apparatus weighs 20 to 25 g and will hold 35 g of soda lime [7] and 7 g of calcium chloride. It will absorb 10 g or more of carbon dioxide without renewal. The second soda-lime tube contains alumina [8] in its second arm, which, it is thought, dries the gas to a degree comparable, for the purposes of the present work, to the drying by the concentrated sulphuric acid which precedes the soda-lime apparatus. To be certain that complete combustion is obtained, the gas finally passes through a faintly yellow solution of palladium chloride in water. While using the apparatus in its present form it has not been necessary to renew the palladium chloride solution, no sign of reduction having appeared in a number of combustions. The sulphuric acid-bichromate solution must be renewed in the first U-tube after every two or three analyses, while the zinc will last for a larger number of determinations.

CALCULATION

If 0.5 g sample, and 25 cc out of 50 cc of the acetone solution have been taken, the weight of CO_2 found multiplied by $\frac{136}{440} \times 4 \times 100 = 123.6$ gives the percentage of $C_{10}H_{16}$ on the basis of $C_{10}H_{16} = 10CO_2$.

TIME REQUIREMENTS

For a single nitration about 15 minutes per sample is necessary; for the combustion, 30 to 45 minutes. Analyses of samples ground up in the forenoon of one day are completed the next. With one combustion tube two analyses may be run per day along with other work, while by using two tubes it is thought that, after some proficiency has been acquired, as many as four determinations can be made per day.

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[7] The J. T. Baker Chemical Co. furnishes a 12-mesh soda lime containing 15 per cent water, prepared for carbon dioxide absorption.

[8] F. M. C. Johnson, J. Am. Chem. Soc., 34, p. 911, 1912.

FORMATION OF CARBON DIOXIDE FROM THE RUBBER DURING NITRATION

It is claimed by Alexander [9] that during the formation of the nitrosite and nitrosate of rubber large quantities of carbon dioxide are evolved from the oxidation of the rubber by the nitrogen oxides. Gottlob,[10] on the other hand, found only very small amounts of carbon dioxide. The writer made several tests of this important point by passing the gases from the rubber solution into a large volume of clear, saturated baryta water. Fine Para rubber, previously extracted with acetone and dried, was used for the experiments. After the chloroform, cooled as in the analytical procedure, had attained the deep green color, the apparatus was allowed to stand three to four hours, after which a current of carbon dioxide-free air was used to sweep into the barium hydroxide solution any carbon dioxide which might have formed during the interval. Only a trace of barium carbonate, a slight ring in the delivery tube, was formed, although the barium hydroxide solution remained alkaline throughout the experiment.

DETERMINATION OF THE SULPHUR OF VULCANIZATION

If the statement of Alexander [11] proves to be true that the sulphur of vulcanization of the rubber remains quantitatively in the nitrosite, this method could possibly admit of the simultaneous determination of the sulphur of vulcanization. An aliquot portion of the clear acetone solution of the nitrosite would be evaporated to dryness and the sulphur determined in the usual way.

RESULTS

The following results were obtained by the method above described. All are given that have been obtained on good quality, soft-vulcanized compounds since the date after which no great changes in the procedure were made. Whether the method is applicable to compounds of poor quality has not been determined, and as the author is no longer in a position to work on this point

[9] Zs. angew. Chem., **20**, p. 1358, 1907; **24**, p. 684, 1911.
[10] Ibid., **20**, p. 2213, 1907.
[11] Ibid., **20**, p. 1364, 1907; **24**, p. 687, 1911; Ber., **40**, p. 1077, 1907.

the field must be left to others. This Bureau may be able, however, to work in this field at some later date.

A. A washed and dried up-river fine gave 94.0, 95.1, 95.8, and 95.9 per cent $C_{10}H_{16}$. Avg.=95.2 per cent plus 3.3 per cent acetone extr.=98.5 per cent.

B. A commercial compound containing 45 per cent fine Para gave 42.0, 42.2, 42.7, 43.1, 43.3, and 43.4 per cent $C_{10}H_{16}$. Avg.=42.8 per cent plus 1.3 per cent acetone extr.=44.1 per cent.

C. A commercial compound containing 48 per cent fine Para gave 44.8, 45.1, 45.1, and 45.3 per cent $C_{10}H_{16}$. Avg.=45.1 per cent plus 2.4 per cent acetone extr.=47.5 per cent.

D. The same compound after standing finely ground for a month gave 43.4, 43.5, 43.5, and 45.0 per cent $C_{10}H_{16}$. Avg.=43.7 per cent.

E. A commercial compound containing 25 per cent fine Para and 20 per cent caucho or 45 per cent gum gave 40.3, 40.4, 40.6, and 41.1 per cent $C_{10}H_{16}$. Avg.=40.6 per cent plus 3.2 per cent acetone extr.=43.8 per cent.

F. A commercial compound containing 41.5 per cent coarse Para gave 39.5, 39.6, 39.8, and 40.1 per cent $C_{10}H_{16}$. Avg.=39.8 per cent plus 2.1 per cent acetone extr.=41.9 per cent.

SUMMARY

A new method for the direct determination of rubber is described, which is based upon the combustion of the nitrosite of rubber in a current of oxygen and weighing of the carbon dioxide thus formed. The results indicate a fair degree of reliability for both raw rubber and high-grade vulcanized compounds. The use of this method for the analysis of low-grade compounds and for the simultaneous determination of sulphur of vulcanization may be possible if its application to these fields is further studied.

During this work many valuable suggestions were made by Dr. W. F. Hillebrand, Mr. J. B. Tuttle, and a number of others at this Bureau, and I take this opportunity to express to them my appreciation of the same.

WASHINGTON, February 13, 1914.

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No. 36

INDUSTRIAL GAS CALORIMETRY

BY

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Bureau of Standards

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INDUSTRIAL GAS CALORIMETRY

C. W. Waidner and E. F. Mueller

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I. OBJECT AND SCOPE OF THE INVESTIGATION

The first laws and regulations adopted by cities, and later by States, related to the photometric requirements which manufactured gas must fulfill. With the increasing applications of gas to heating and power purposes, and to mantle lighting, the importance of the heating value of the gas began to be realized. It has been estimated that at the present time over 80 per cent of the gas distributed in the United States is applied to the purposes stated above, and perhaps as much as 90 per cent in many cities. The tendency of recent legislation [1] and regulation has therefore been toward the adoption of either a double standard, including both an illuminating value and a heating value standard, or, in many instances, the adoption of a standard heating value alone.

In view, therefore, of the increasing importance of the measurement of the heating values of gases, the object of the present investigation was an experimental study of the leading types of gas calorimeters that are widely used in the gas industries, in order to furnish gas engineers, public-service commissions, and gas inspectors exact information as to the accuracy attainable with the instruments, the sources of error to which they are liable, and the important precautions that should be observed in their use in order to obtain reliable results.

The committee on calorimetry of the American Gas Institute has for several years been conducting a series of valuable tests on gas calorimeters, the results of which are contained in several reports to the institute,[2] and the careful reading of these is recommended to those interested in gas calorimetry. The necessity of the present investigation was urged by J. B. Klumpp, chairman of the committee, and by many other eminent gas engineers, with a view to obtaining independent evidence on the conclusions arrived at by the committee, and with a view to considering some of the problems that could not be taken up by the committee in the time at the disposal of its members. The investigation was also made necessary at this time by the fact that the

[1] A review and discussion of laws and regulations relating to gas will be found in Circular of the Bureau of Standards, No. 32, "Standard regulations for manufactured gas and gas service."

[2] Proc. Am. Gas Institute, **3**, 285, 1908; **4**, 148, 1909; **7**, 65, 1912.

Bureau was being called upon by public-service commissions and others to test calorimeters of various types.

The calorimeters included in this investigation are enumerated in Table 1. All of the calorimeters are of the flow type except the Parr, which is of the comparison type.

TABLE 1

List of Calorimeters Investigated

Calorimeter	Maker
Junkers, original type	Junkers & Co., Dessau, Germany.
Junkers, new type	Do.
Hinman-Junkers	American Meter Co., New York, N. Y.
Sargent	Sargent Steam Meter Co., Chicago, Ill.
Simmance-Abady, English type	Alex. Wright & Co. (Ltd.). Westminster, London, England.
Simmance-Abady, American type	Precision Instrument Co., Detroit, Mich.
Boys	John J. Griffin & Sons, London, England.
Doherty	Improved Equipment Co., New York, N. Y.
Parr	Standard Calorimeter Co., E. Moline, Ill.

With a view to making the results of this investigation available to those who have not had a special technical training, the matter is presented in somewhat greater detail than would be strictly necessary for the scientific reader. However, in order not to unduly extend the length of this report, only the conclusions, based on a vast amount of experimental data, have in many instances been given, and only sufficient data have been given here and there throughout the report to familiarize the reader with the experimental methods employed in investigating the various questions that have been considered.

The methods of operation which this and other investigations have shown to be suitable for the various calorimeters are given in the section on "Measurement of heating values," in Bureau of Standards Circular No. 48, in the form of detailed operating directions. The section referred to also contains other matters of interest in connection with the equipment of a calorimetric laboratory. Tables to be used in connection with heating-value determinations are also included in the circular.

The more important conclusions of this investigation are briefly summarized on pages 39 to 40, and 148 to 150.

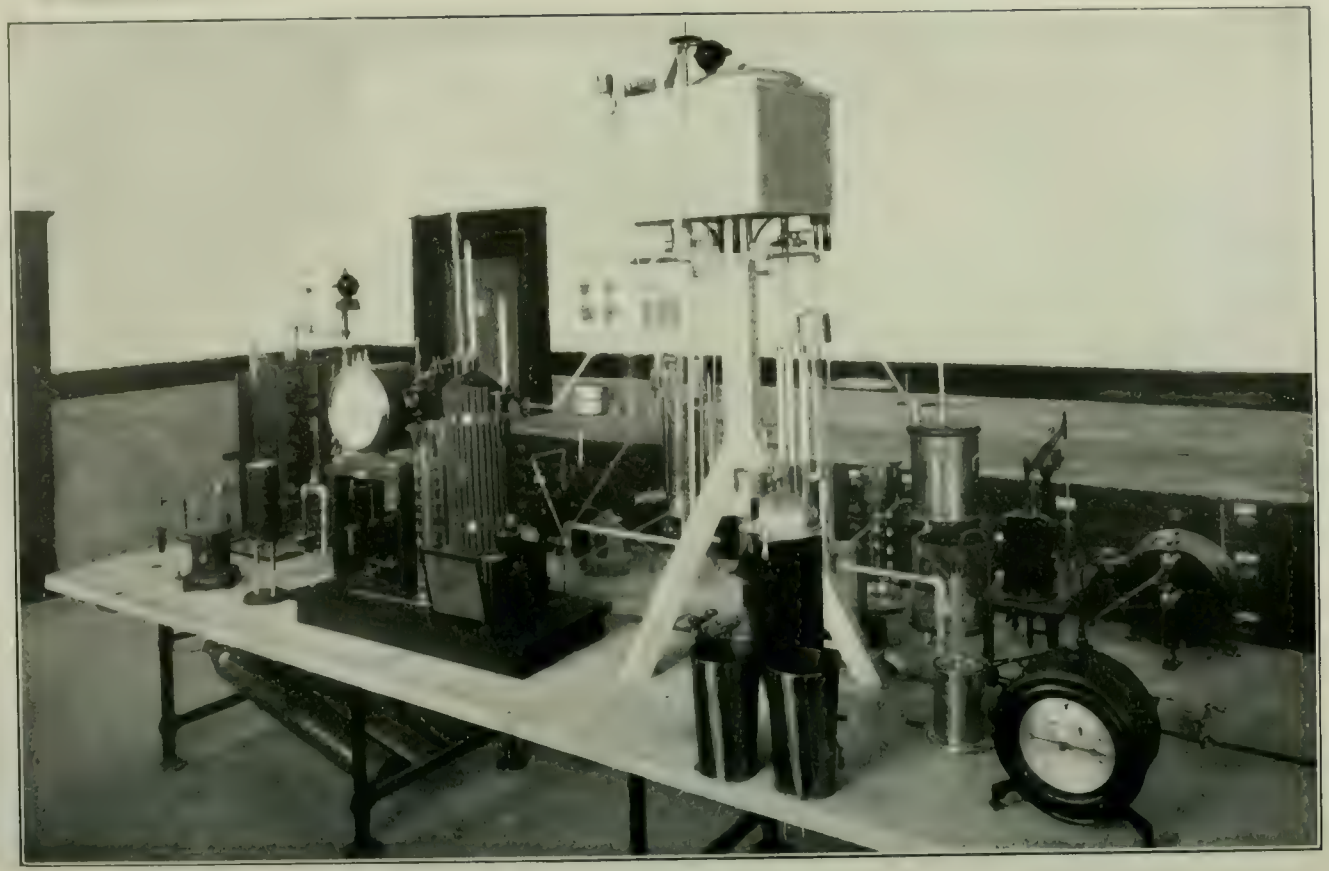

Fig. 1. *View of calorimetric laboratory*

II. LABORATORY [3] EQUIPMENT

GAS SUPPLY

There was available for this investigation a 5 cubic-foot meter prover, which was used as a gas tank for drawing from the laboratory gas mains samples of the gas to be used in testing the calorimeters and similarly for holding the samples of natural gas and of hydrogen used in intercomparing the different calorimeters.

The gas connections used will be understood by reference to Fig. 2. Gas from the mains passes through the pressure regulator A, the meter B, the three-way stopcock C, another regulator D, and to the burner in the calorimeter. An unlimited supply of gas, of approximately the same heating value as that in the holder, was thus available for bringing the calorimeter to equilibrium,

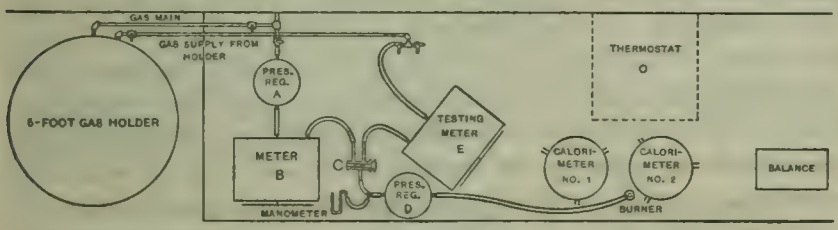

Fig. 2.—*Diagram of gas connections*

adjusting the rate of gas consumption, etc. When a test was to be made the three-way stopcock was turned, causing the gas to flow from the gas holder through the testing meter E to the burner. With this arrangement as many as 12 separate determinations of heating value could be made with one holder full of gas, and the conditions between tests could be varied as desired. Further, during such a series of determinations, only the amount of gas used in the tests was passed through the testing meter, thereby diminishing the possibility of change in the water level in the meter during the experiments. In any such series of determinations the last tests were made under conditions identical with the first tests, so as to determine whether any changes had taken place during the series, as, for example, a change in the heating value of the gas drawn from the holder.

[3] A general view of the laboratory is shown in Fig. 1.

Calorimeters which were to be compared were set up so that the gas supplied through the system described could be burned in the two alternately, giving the most favorable conditions for determining any difference in heating values as measured with the two calorimeters.

WATER SUPPLY

At some distance above the table in Fig. 1 is shown a thermostatically controlled water bath from which water at constant temperature was delivered to the calorimeters.

The principle of action of this thermostat is briefly as follows: Water from the house piping is delivered into the thermostat slightly in excess of that drawn from it by the calorimeters, the excess being passed to drain through an overflow. Within the thermostat is a helical coil filled with an expansible liquid which, acting on a mercury U gauge, makes and breaks an electric circuit in which is an electromagnet, on the movable arm of which is a bucket. There is a second delivery pipe which discharges into the thermostat a stream of hot water in excess of that required to bring the thermostat to the desired temperature. When the temperature of the water in the thermostat attains that for which the mercury contact is set the electromagnet is operated and the bucket is moved under the stream of hot water, which is thus diverted to drain. The supply of hot water being cut off, the temperature falls, the electric circuit is interrupted, hot water is again delivered into the thermostat, etc.

When the temperature of the water in the house piping was already above that to be delivered by the thermostat, which was the case in summer, the hot-water supply was replaced by a cooled-water supply.

To insure thorough mixing of the two streams of water delivered into the top of the thermostat, these streams were delivered into a brass tube, extending from a short distance below the upper surface of the water nearly to the bottom, in which tube was mounted a motor-driven stirrer of the propeller type.

This thermostat would deliver to the calorimeters water the temperature of which was constant to 0°.01 or 0°.02 F for long periods. The importance of using water at constant inlet temperature will be recognized when it is remembered that a change

of temperature of the inlet water does not make itself manifest at the calorimeter outlet until some time after the change has taken place, so that considerable error may result if the temperature of the inlet water varies much during the progress of a heating-value test, although this error may be diminished by proper procedure. (See p. 45.)

OTHER EQUIPMENT

Other items of equipment were a Rueprecht equal-arm balance; flow calorimeters enumerated on page 6; experimental wet meters of the American Meter Co., Elster, Sargent, Griffin, and Alexander Wright makes; a one-tenth cubic foot bottle; several complete calorimeters of the Berthelot bomb type with all accessories, such as calorimetric resistance thermometers, special resistance bridges, etc.; an Assmann aspiration psychrometer; a Fuess standard barometer; several wet pressure regulators of different types; weighing buckets; graduates; thermometers; gas tanks; etc. The laboratory table with stone top was provided with gas, compressed air, vacuum, hot-water, cold-water, and ice-water outlets, drain connections, and electric wiring.

III. HEAT UNITS AND HEATS OF COMBUSTION

HEAT UNITS

A quantity of heat is usually measured by the change in temperature which it can produce in a known mass of water. The heat unit is, therefore, defined as the quantity of heat required to raise the temperature of unit mass of water one degree. As the specific heat of water is not a constant but varies slightly with the temperature, it is further necessary, in precise scientific work, to specify the temperature of the water. Although the heat unit has not been defined by any international congress, it has become the general custom to express quantities of heat in terms of water at 15° C (59° F). More recently a preference has been shown, for a number of reasons, for a calorie defined in terms of the capacity for heat of water at 20° C, or even at a higher temperature. The difference between the 15° and the 20° calorie is negligible for the purposes of industrial gas calorimetry and the former has been retained in the present report.

The units in which the heating values (or heats of combustion) of fuels, foods, explosives, etc., are expressed are: (*a*) the (small) *calorie;* (*b*) the (large) *Calorie;* and (*c*) the *British thermal unit*, designated briefly Btu.

The calorie is the quantity of heat required to raise the temperature of 1 gram of water 1° at 15° C.

The Calorie is the quantity of heat required to raise the temperature of 1 kilogram of water 1° at 15° C.

On the same basis the British thermal unit is the quantity of heat required to raise the temperature of 1 pound of water 1° at 59° F.

For converting quantities of heat expressed in terms of any one of the heat units defined above to quantities of heat expressed in terms of either of the other two heat units, the following are the conversion factors:

1 Calorie = 1000 calories;

1 British thermal unit = 252.0 calories.

For the order of accuracy required, or readily attainable, in nearly all engineering or industrial tests, the variation of the specific heat of water in the range of temperatures within which calorimetric experiments are conducted is so small that it may be neglected. For example, the amount of heat required to raise the temperature of a given mass of water 1 degree at 35° C (95° F) is about 1 part in 500 (0.2 per cent) smaller than that required at 15° C (59° F).

The specific heat of water has been the subject of elaborate investigations by numerous experimenters, but there is considerable discrepancy between the various published values. Table 2 is given to show the order of magnitude of the variation of the specific heat of water with temperature. The values given were obtained by inspection of the data summarized by Börnstein and Scheel in the Landolt-Börnstein-Roth Physikalisch-Chemische Tabellen, Table No. 171, page 760, and are sufficiently accurate for the purposes of industrial gas calorimetry.

As tap water is used for measurements with flow calorimeters, it is of interest to estimate what degree of impurity is of significance in such measurements. Examination of published data on the specific heats and the densities of dilute solutions shows that for the class of soluble matter likely to occur in city water supplies

an increase of 1 per cent in the density will cause a diminution of the specific heat of about 2 per cent. Hence, if the error in the calorimetric measurement due to impurities of this kind in the tap water is not to exceed 0.1 per cent, the density of the tap water should not differ from that of pure water by more than 0.05 per cent if the water is weighed in the calorimetric test, or by more than 0.1 per cent if the water is measured volumetrically. The error in a calorimetric measurement, due to the effect of impurities on the specific heat of water, is less if the water is measured than if it is weighed, because the volume specific heats of the dilute solutions here considered vary less rapidly with concentration than do the mass specific heats. As measurements of specific heats present great experimental difficulties, while density determinations to the required accuracy are readily made, a criterion of the purity and therefore of the specific heat of the water is most simply obtained from density measurements.

TABLE 2

Specific Heat of Water at Various Temperatures in Terms of the Specific Heat at 15° C Taken as Unity

Temperature	Specific heat
°C	
5	1.004
10	1.002
15	1.000
20	.999
25	.998
30	.998
35	.998

The specific heat of the tap water used in the present series of experiments differed from that of pure water by much less than 0.1 per cent, as shown both by density measurements and by determinations of the specific heat in other calorimetric researches.

HEATS OF COMBUSTION

In formulating a precise definition of the heat of combustion of a substance, it is necessary to specify the following:

(*a*) What compounds are to be formed from the elements which the substance contains when the substance combines with oxygen.

(*b*) The quantity and the initial state (solid, liquid, or gaseous) of the substance. If the substance be a gas, the quantity contained in a given volume will depend on the temperature and pressure of the contained gas. Hence, in order that the term "heat of combustion of a gas" may have a definite meaning, the volume of the gas must be referred to some standard temperature and pressure. In scientific work the volume of the gas is reduced to what it would be at 0° C and under 760 mm pressure (standard gravity). In industrial and engineering work, where water vapor enters into the composition of the gas, it is also necessary to specify the water vapor content of the gas. In engineering tests and for the purpose of the industrial testing and measurement of gases the standard temperature and pressure almost invariably used in the United States are 60° F and 30 inches of mercury, and the gas, for purposes of testing, is saturated with water vapor.

(*c*) The number of heat units produced by the combustion of the given quantity.

(*d*) The conditions (constant pressure or constant volume) under which combustion takes place.

(*e*) The initial temperature of the substance and oxygen (or air) and the final temperature of the products. It is not sufficient to specify merely that these temperatures shall all be equal, since, on account of the difference in the heat capacity of the substance plus oxygen and that of the products, the amount of heat produced by the combustion will depend, to a small extent, on the temperature chosen.

(*f*) The pressure, if the combustion takes place at constant pressure. This is for reasons similar to these given for (*e*), above. Naturally, in defining the heat of combustion the initial temperature chosen would be that for which the heat unit is defined and the constant pressure chosen would be the standard atmospheric pressure.

(*g*) The states, solid, liquid, or gaseous, to which the various products are reduced.

The following general definition is formulated in accordance with the requirements outlined above:

The heat of combustion, at constant pressure, of a gas containing only the elements, or compounds of the elements, carbon, hydro-

gen, oxygen, and nitrogen, is the number of heat units produced by the combustion of unit quantity of the gas initially at a specified temperature and at standard atmospheric pressure, with oxygen at the same temperature and pressure, with formation of gaseous carbon dioxide and nitrogen and liquid water, all cooled to the initial temperature and at standard atmospheric pressure; unit quantity of the gas being the quantity which would occupy unit volume at the standard temperature and standard pressure chosen for gas measurement.

A definition of this type is, however, too complicated for engineering or industrial use. A simpler and quite satisfactory definition can be formulated by omitting reference to (*a*), the omission being more or less supplied by the use of the term "combustion" and by explicitly omitting (*e*) and (*f*), so that, in such a definition, no account is taken of the temperature or pressure coefficients of the reactions. In testing complex mixtures, such as illuminating gas, it is difficult to calculate the coefficients, and in any case no significant difference would be introduced by neglecting them.

For the reasons outlined above, the following definitions are sufficiently precise for engineering and industrial use:

The *total heating value* of a gas, expressed in the English system of units, is the number of British thermal units produced by the combustion, at constant pressure, of the amount of the gas which would occupy a volume of 1 cubic foot at a temperature of 60° F, if saturated with water vapor, and under a pressure equivalent to that of 30 inches of mercury at 32° F and under standard gravity, with air of the same temperature and pressure as the gas, when the products of combustion are cooled to the initial temperature of gas and air and when the water formed by combustion is condensed to the liquid state.[4]

[4] The definition of the total heating value of gas adopted by the American Gas Institute (Proc., 8, p. 385; 1908) is as follows: "The heating value of a gas is the total heating effect produced by the complete combustion of a unit volume of the gas, measured at a temperature of 60° F and a pressure of 30 inches of mercury, with air of the same temperature and pressure, the products of combustion also being brought to this temperature." This definition does not call attention to the fact that the condition of saturation with water vapor of the gas must be defined. The pressure of 30 inches of mercury is not definite unless the temperature of the mercury be also specified. The definition does not distinguish between total and net heating value, since it fails to specify whether the water formed in combustion is to be in the form of liquid or of vapor, when the products are cooled to the initial temperature.

The *net heating value* of a gas, expressed in the English system of units, is the number of British thermal units produced by the combustion, at constant pressure, of the amount of the gas which would occupy a volume of 1 cubic foot at a temperature of 60° F, if saturated with water vapor and under a pressure equivalent to that of 30 inches of mercury at 32° F and under standard gravity, with air of the same temperature and pressure as the gas, when the products of combustion are cooled to the initial temperature of gas and air and the water formed in combustion remains in the state of vapor.

According to the above definitions the net heating value is less than the total heating value by an amount of heat equal to the latent heat of vaporization, at the initial temperature of the gas and air, of the water formed by the combustion of the gas.

For most calorimetric calculations the heat of vaporization of water may be taken as being equal to 580 calories per gram, corresponding to 2.3 Btu per cc (graduates are almost invariably calibrated in cc).

In addition to the terms "total heating value" and "net heating value," the term "*observed heating value*" will be used, as a matter of convenience, in discussing the experimental data. The observed heating value for a flow calorimeter will be understood to be the value obtained by multiplying the mass of water which flowed through the calorimeter during the test by the corrected rise in temperature of the water, and dividing by the volume (referred to the standard conditions of 60° F and 30 inches) of gas burned.

It has been the general practice to regard the observed heating value as identical with the gross (total) heating value. This practice is not permissible if an accuracy better than 2 or 3 per cent is required, since even with a perfect flow calorimeter these two heating values would necessarily differ by 2 per cent or more under certain atmospheric conditions (e. g., 10 per cent humidity and 90° F; see Table 19), while for some of the calorimeters tested the difference might amount to about 4 per cent.

In view of the fact that the term "gross heating value" was intended to mean total heating value, but has generally been

applied to the observed heating value as well, it seems desirable to discontinue the use of the term "gross heating value." If the term "total heating value" is adopted, strict consistency of nomenclature might require the discontinuance of the use of the term "net heating value" and the use of "partial heating value" in its stead. This practice has not been followed in the present report.

The heating values found with well-designed flow calorimeters (after the necessary corrections are applied for loss of heat to surroundings, heat carried off in products, etc.) are the total heating value and the net heating value defined above. The heat of combustion directly found with calorimeters of the Berthelot bomb type is the total heat of combustion under the condition of constant volume. The difference between the heat of combustion at constant pressure and at constant volume is due to the work done by the external pressure on the products of combustion, and is measured by the product of this pressure and the change in volume of the gases taking part in the reactions. If the change in volume due to the reaction is known or if the composition of the gas is known, so that the change in volume may be calculated, the heat of combustion expressed under either condition may be reduced to the other.

IV. TYPES OF CALORIMETERS

Many types of calorimeters have been suggested and used to measure heats of combustion of gases.

(*a*) In the Berthelot bomb type the combustion takes place at constant volume within a bomb in the presence of sufficient oxygen to insure complete combustion. This type of calorimeter gives the total heat of combustion at constant volume.

(*b*) In the Regnault and Julius Thomsen types the gas is burned in a combustion chamber within the calorimeter and the products of combustion are caused to give up their heat by being passed through a worm immersed in the water of the calorimeter.

(*c*) In the comparison type, such as the Parr gas calorimeter, the rise in temperature produced in a calorimeter by the combustion of a given volume of the gas is compared with the rise in temperature produced in a similar calorimeter by the combustion of a

known volume of a gas the heat of combustion of which is known. In a restricted sense the Strache calorimeter is an instrument of this type.

(*d*) The water-flow type is utilized most frequently for the calorimetry of gases and is exemplified in the calorimeters listed on page 6, with the exception of the Parr calorimeter. The principles of the flow calorimeter are discussed in the following section:

(*e*) A large number of gas calorimeters have been devised, the operation of which depends upon the indications of some thermometric device, heated by gas burned at a constant rate as controlled by a pressure regulator or other regulating mechanism. The thermometric device may be thermoelectric or may depend upon the expansion of a solid, of a liquid, or of a gas. The Fery calorimeter, the Fahrenheim, the Smith, and the Sarco recording calorimeters and the Simmance-Abady calor-graph are calorimeters of this type. In another class of calorimeters a definite quantity of gas is burned in the apparatus and the heating value of the gas deduced from the change of temperature of a mass of material subjected to the action of the flame. The Graefe and the Raupp calorimeters are of this type. The indications of these calorimeters are arbitrary and they must be calibrated by comparison with a standard calorimeter. Since the products of combustion escape from such calorimeters at relatively high temperatures, these instruments are usually calibrated for indicating or recording net heating values.

In all of the types described, except (*a*), the combustion takes place under the condition of constant pressure. Calorimeters of types (*b*), (*c*), and (*d*) are used to measure the total heat of combustion at constant pressure, and when suitably constructed some of them may be used to measure the net heat of combustion at constant pressure. Calorimeters of type (*d*) have been used in connection with recording devices to obtain continuous records of total heating values.

The reader will find descriptions of numerous calorimeters in the publications of Immenkötter [5] and of Coste.[6]

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[5] Über Heizwerthbestimmungen mit besonderer Berücksichtigung gasförmiger und flüssiger Brennstoffe, published by R. Oldenbourg, Munich and Berlin.

[6] The Calorific Power of Gas, published by Chas. Griffin & Co. (Ltd.), London.

V. PRINCIPLES OF FLOW CALORIMETRY AND DETERMINATION OF TOTAL AND NET HEATING VALUES

In flow calorimeters the heat to be measured is imparted to a stream of water, the mass of water flowing through the calorimeter during the time that a known mass or volume of the combustible is burned within the calorimeter and the resulting change in temperature of the water, furnishing the data necessary for calculating the heat imparted to the water. There are always, however, some losses of heat from the calorimeter, the magnitude of which must be determined in order that suitable corrections may be applied to the observed heating value, if such losses are large enough to be of significance for the accuracy that is sought.

The details of construction of various makes of flow calorimeters are shown in the illustrations and sectional drawings included in this report. The gas, the heating value of which is to be determined, is measured with a suitable wet meter, and is burned at a constant rate in a suitable burner within a nearly closed chamber called the combustion chamber. The air necessary to support the combustion enters the combustion chamber through the open bottom of the calorimeter, the circulation through the calorimeter being induced by the heated products of combustion. Under some conditions (e. g., open damper, small rate of gas consumption) the air drawn through the calorimeter is very considerably in excess of that required for combustion, while at high rates of combustion the air supply may be insufficient to insure complete combustion.

The heated products [7] pass up through the combustion chamber, which is surrounded by the flowing water, then downward through tubes or spaces also water cooled, and finally are discharged into the atmosphere through an outlet in which a damper, by which the amount of air drawn through the calorimeter may be controlled, is usually placed. The heated gaseous products are thus made to impart to the water flowing through the calorimeter nearly all the heat resulting from combustion.

[7] As a matter of convenience the gases discharged from the calorimeter, which include practically all of the products of combustion except the water condensed in the calorimeter, as well as the nitrogen and excess oxygen from the entering air, will be referred to as the products of combustion, or often simply as the products.

The temperature of the water entering and leaving the calorimeter is measured by the inlet and outlet water thermometers, respectively. A mixing device should be provided to thoroughly mix the heated water before it reaches the bulb of the outlet-water thermometer in order that this thermometer shall indicate the true mean temperature of the effluent water. The water flows through the calorimeter under a pressure determined by the difference in level of the inlet and outlet overflow wiers. The rate of flow of water, and hence its rise of temperature, may be varied by a suitable valve.

The determination of the heating value of a gas by means of a flow calorimeter was carried out as follows: Gas was burned at the proper rate (as measured by the gas meter) and with proper air supply (controlled by the damper) in a suitable burner placed within the combustion chamber of the calorimeter; the rate of flow of water through the calorimeter was so adjusted (by the valve) that the rise of temperature of the water was the desired amount (usually 15° to 20° F); the temperature of the water was so regulated that it entered the calorimeter at approximately room temperature; after the gas had been burning long enough for a condition of thermal equilibrium to be set up in the calorimeter, observations were begun by reading (*a*) pressure, temperature, and humidity of air; (*b*) temperature of products of combustion; (*c*) temperature of gas meter and the gas pressure at meter inlet; (*d*) series of readings of inlet and outlet water thermometers; (*e*) weight or volume of water which flowed through the calorimeter during the combustion of the chosen volume of gas (usually two turns of the one-tenth or one-twelfth cubic foot meter).

Two or three readings of the outlet-water thermometer were taken before the index of the gas meter passed through its zero position; at this instant the change-over device, into which the water discharged from the calorimeter, was shifted to divert the water from drain to measuring vessel. Observations of the readings of the outlet-water thermometer were then made at frequent and regular intervals until the index of the meter had made nearly two complete revolutions (i. e., until $2 \times \frac{1}{10}$ or $2 \times \frac{1}{12}$ cubic feet of gas had been burned). The instant the index of the meter passed

through zero, on completion of its second revolution, the change-over device was shifted, diverting the water from measuring vessel back to drain. One or two more readings of the outlet-water thermometer and one more reading of the inlet-water thermometer were taken and then the water collected was weighed.

The readings of the outlet-water thermometer before and after shifting the change-over device were taken simply to show that steady conditions had been maintained before and after the test.

The barometric pressure was read to enable the volume of gas burned during the experiment, as measured by the meter, to be reduced to standard conditions, and the humidity of the air of the room was determined by a suitable wet and dry bulb psychrometer of the aspiration type to enable the correction to be applied to reduce the observed heating value to the total heating value, as hereinafter explained.

The observations above referred to, all of which may be taken in a few minutes, contain all the data necessary for a single determination of the total heating value of the gas burned in the calorimeter. For calculating the net heating value of the gas the amount of water vapor condensed out of the products of combustion of a known volume (1 cubic foot is sufficient) of the gas was collected and measured in a 25-cc graduate placed under the drip tube at the base of the calorimeter. The collection of this condensate for purposes of measurement should obviously not be started until the gas has been burning in the calorimeter long enough to insure that the inner walls and tubes of the calorimeter have become uniformly wetted and the drainage therefrom has become uniform.

The accuracy with which the various operations incident to the determination of the heating value of a gas can be carried out are considered in detail in later sections. It will probably assist in reading what follows to anticipate some of the experimental results discussed in detail later and consider at this point the various heat losses from one of these flow calorimeters and give an example of the observations necessary and the mode of calculation used to find the corrected total and net heating values of a gas.

Assuming for the present that the type of burner and the air supply are such that the combustion is complete, then, in an efficient calorimeter, all but a small proportion of the heat produced in the combustion chamber is communicated to the water flowing through the calorimeter, and is thus measured by the product of the quantity of water flowing through the calorimeter and the resulting rise in temperature of the water.

The combustion products escape from the calorimeter at a temperature slightly above that of the inlet water, which for the present is assumed to be at room temperature. If the products escape at a higher temperature, they carry off some sensible heat which, however, is rarely as much as 0.1 per cent of the heat measured. These products, however, are saturated or nearly saturated with water vapor at the temperature at which they escape from the calorimeter, and if a large amount of relatively dry air is drawn into the calorimeter, the escaping products will carry off considerable amounts of water vapor taken from the water produced by the combustion; that is, a considerable correction will be necessary to allow for the heat of condensation thus lost from the calorimeter. The magnitude of this correction will evidently depend upon the volume of air taken into the calorimeter, the volume of the products, and the temperatures and degrees of saturation of the entering air and gas and of the escaping products. Hence, it will be seen that the observed heating value for a given sample of gas will depend upon the humidity of the air at the time of the experiment.

Another source of error is the heat interchange between the calorimeter and the room, due to the fact that the average temperature of the surface of the calorimeter differs from that of the room. The heat interchange may conveniently be considered as made up of two parts—(*a*) that due to the excess of the average temperature of the surface above that of the inlet water and (*b*) that due to the difference between inlet water temperature and room temperature.

Suitable corrections were applied to the observed barometric pressure, the readings of the psychrometer thermometers, the gas-meter thermometer, the inlet and outlet water thermometers,

the combustion products thermometer, and to the observed weight of water. However, sufficiently accurate thermometers can be obtained for the psychrometer, the barometer, the gas meter, and the products so that the corrections may be neglected. Sets of weights and balances can also be obtained of such accuracy that their errors are negligible. The only significant correction to the weighings is then the so-called reduction to vacuo (see p. 90), which amounts to about 1 part in 1000 of the weight of water.

If the Btu is defined in terms of water at 60° F and the mean temperature of the water during the test is 90° F, a correction would be required, due to the variation of the specific heat of water, amounting to about 0.2 per cent. In routine gas testing the application of corrections for reduction to vacuo and for variation of the specific heat of water may be omitted, since both corrections are small and, for the usual conditions under which flow calorimeters are used, are of opposite sign and tend to neutralize one another.

The complete data and reductions for the determination of the total and net heating values of a sample of gas are given in Table 3. This is not an exact copy of the laboratory records. All measurements in this investigation were made in the metric system of units (liters, grams, °C). A record form to be used in routine testing may be found in Bureau Circular No. 48.

TABLE 3

Observed Data and Computation for a Determination of Total and Net Heating Values

	Inlet thermometer #5808A	Outlet thermometer #5808C		
Gas not burning	$85°46$	$85°46$	(c) Products $=85°8$	(f) Barometer
			Meter $=85°6$	$85°6$ 29.80 ins.
			Gas pressure at meter inlet=1.5 ins. water	Scale and index .00
Certif. cor.	+.04	+.06		Gravity −.02
				Temp. −.14
	85.50	85.52		Cor. bar. 29.64
			(d) Gas rate 6.9 cu. ft. per hour, damper closed.	Gas pres. .11
				Pres. on gas 29.75
∴Apply a differential correction of −0°02 to readings of outlet thermometer (a)			(e) Condensed water collected for 7 turns of meter=12.5 cc; condensate per cu. ft. =19.4 cc	(g) Psychrometer
	85.46	$103°43$	Weight of water 6.708 lbs.	Dry bulb $85°6$
		.50	Reduction to vacuo +.007	Wet bulb $69°8$
		——— b		∴Humidity=45%
		.50	Cor. to weights .000	
		.46	Mass of water =6.715 lbs.	
		.43		
		.46	(h) Volume of gas Meter No. 6312	
		.43	2 turns of meter 0.2000 cu. ft.	
		.50	Cal. cor. (0.53% slow) +.0011	
		.51	Vol. delivered at $85°6$ and 29.75 ins. 0.2011 cu. ft.	
		1 turn→	∴Vol. at 60° and 30 ins. =0.1854 cu. ft.	
		.55		
		.60	Observed htg. value $=\frac{6.715\times 18.23}{0.1854}=660.3$ Btu	
		.53	(d) Correction for atmospheric humidity +5.0 "	
		.51	(i) Radiation correction +0.8 "	
		.50		
		.60		
		——— b		
		.59	(j) Cor. for var of sp. heat of water (to reduce to 60° F Btu) −1.3 "	
	85.46	.51		
	85.46	103.51	(k) ∴Total htg value =665 Btu.	
Certif. cor.	+.04	+.13		
Stem cor.	[illegible]	+.11	Obs., htg value 660.3 Btu	
Differential cor.		−.02	(e) Cor. for 19.4 cc of condensate −44.6 "	
			(i) Cor. for radiation +0.8 "	
	85.50	$103°73$	(j) Cor. for sp. heat of water (to reduce to 60° F Btu) −1.3 "	
		$85°50$		
∴Corrected temp. rise.....		$-18°23$	(l) Net heating value =615 Btu.	

Temperature controlled by thermostat.

EXPLANATORY NOTES TO TABLE 3

(a) When no gas was burning the readings of the inlet and outlet water thermometers, corrected by the certificate corrections, would have been equal if no changes had taken place in the thermometers since they were tested and if there had been no heat interchange between the calorimeter and its surroundings. The

VI. MEASUREMENT OF GAS VOLUMES—INVESTIGATION OF LABORATORY TYPE OF GAS METERS

Inasmuch as the measurement of gas volumes enters directly into all tests of the heating values of gases an investigation of the accuracy with which such measurements could be made and of the sources of error affecting them was a necessary preliminary to the investigation of the calorimeters.

1. REDUCTION TO STANDARD PRESSURE AND TEMPERATURE

To make the terms "cubic foot," "liter," etc., of gas definite it is necessary to define not only the volume but also the pressure, temperature, and degree of saturation, with water vapor, of the gas. A measurement of a volume of gas made with any suitable measuring device, at a known pressure, temperature, and degree of saturation, must therefore be reduced to what it would become under some standard conditions of pressure, temperature, and saturation.

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latter condition was secured in this test by adjusting the inlet water temperature to approximate equality with room temperature. If the inlet water temperature is not extremely constant and approximately equal to room temperature, the intercomparison of the thermometers should be made in a pail of well-stirred water rather than in the calorimeter. The differential correction eliminates the error due to relative changes that have occurred in the thermometers since they were tested and certified.

(*b*) Pointer of meter passes through zero position. Change over device shifted to weighing bucket at instant of first passage through zero and back to drain at instant of third passage through zero, so that water collected for weighing corresponds to gas burned during two turns of meter (0.2 cubic feet, approximately).

(*c*) The temperature of the combustion products should, if the calorimeter is operating properly, be very nearly the same as the inlet-water temperature. It is then not necessary to take it into account in the computations.

(*d*) When this calorimeter is operated with the damper closed and illuminating gas is burned at the rate of about 7 cubic feet per hour, approximately 7 volumes of air are drawn into the calorimeter for each volume of gas burned and 6.6 volumes of combustion products are discharged. The correction for atmospheric humidity can therefore be taken from Table 19, page 77.

(*e*) The condensate was measured in a 25-cc graduate divided into 0.5 cc intervals. The latent heat of vaporization of 1 cc=2.3 Btu at the temperature at which gas is ordinarily tested.

(*f*) The usual barometer corrections are applied. The correction to standard gravity is usually omitted, being generally less than 1 in 1000. The temperature correction to reduce the observed barometric pressure to the standard pressure, defined in terms of mercury at 32° F, was taken from a table.

(*g*) An aspiration psychrometer of the Assmann type was used, and the humidity corresponding to the observed readings of the wet and dry bulbs was taken from a table.

(*h*) The meter was calibrated immediately after the experiment by the aspirator-bottle method, fully explained on page 35. This gave the volume delivered for two turns of the meter at the temperature of the meter (85.6°) and at the pressure on the gas in the meter (29.75 inches). The factor for reduction to standard conditions of temperature (60° F) and pressure (30 inches) was taken from a table.

(*i*) This correction for loss of heat to surroundings may usually be neglected. Its magnitude depends on the design of the calorimeter, the rate of gas consumption, and the rise in temperature of the water. This correction is considered on page 52.

(*j*) This correction is generally neglected. It is discussed on page 10.

(*k*) This is the total heating value, as defined on page 13, of the sample of gas tested.

(*l*) This is the net heating value, as defined on page 14, of the sample of gas tested.

The standard temperature and pressure to which measured volumes of gas (saturated with water vapor) are referred, in the United States and in Great Britain, are 60° F and 30 inches of mercury (at 32° F). The correction factors by which the volumes of gas, saturated with water vapor, observed at various temperatures and pressures must be multiplied to reduce to these standard conditions of pressure, temperature, and saturation, may be taken from tables prepared for this purpose.

2. CONSTRUCTION AND MODE OF OPERATION OF METERS

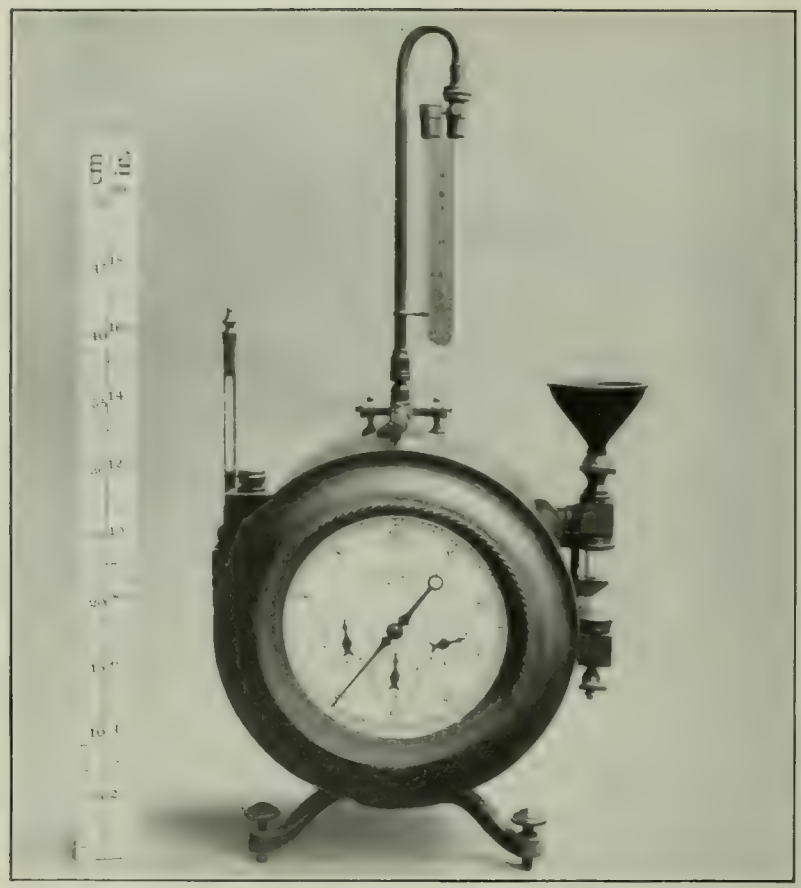
The amount of gas burned in calorimetric and photometric tests is generally measured by small gas meters of the wet-meter type. In some calorimeters (e. g., the Doherty and the Parr calorimeters) the volume of the gas burned is defined by displacing a definite volume of the gas by means of water and forcing the gas thus displaced to flow through the burner in the calorimeter.

The cases of such meters are made of cast iron, steel, or brass, protected by a coating of tin, nickel, japan, or enamel, and sometimes of porcelain.

The dials of these meters are generally graduated so that one complete revolution of the drum, and therefore of the index moving over the dial, corresponds either to one-tenth or one-twelfth cubic foot or to 3 liters. One-twentieth cubic foot meters are also made for inspection work.

Some meters are provided with a second graduated dial on which the rate in cubic feet per hour can be read by one minute's observation. If, however, only a fraction of a turn is read, the results may be considerably in error. (See p. 33.) For this reason photometric meters are usually made to deliver one-twelfth cubic foot per revolution, so that the rate of 5 cubic feet per hour corresponds to one whole revolution of the index in one minute.

The measuring drum of the meter and the shaft and bearings are usually made of some metal or alloy (e. g., tinned brass, Britannia metal, German silver, special bronzes, etc.) which will resist the action of sulphur compounds, ammonia, etc., that may be present in the gas. The stuffing box of the front bearing of the drum is usually accessible by removing the face dial, so that the bearing can be repacked when necessary. In some meters the other bearing is completely surrounded by water.



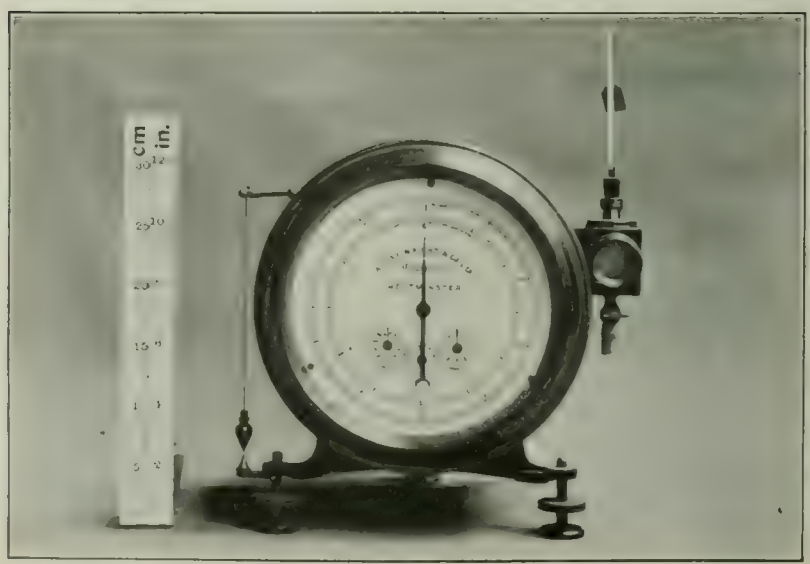


Fig. 3.—*Laboratory gas meters*

To reduce the error in adjusting the water level this adjustment should be made when the drum is in a definite position, e. g., when the index is at zero. The index should therefore be so securely fastened to the shaft of the drum that it can not easily be displaced relatively to it. There are four points in each revolution of the drum when there are considerable fluctuations of the water level and the index should be so mounted on the shaft as to pass through zero about halfway between two such fluctuations.

Descriptions of special features of construction of gas meters may be found in trade catalogues. Two of the meters used in this investigation are illustrated in Fig. 3.

The volume of gas delivered per revolution depends upon the volumes of the compartments of the drum and upon the position of the surface of the water. Hence, it is important that the water level be accurately reproducible. This is secured by mounting the meter on leveling screws, providing it with a suitable level indicator and with a suitable water gauge.

The usual level indicators are (*a*) two spirit levels at right angles, (*b*) circular spirit level, (*c*) plumb bob. The first named is certainly the most convenient to use and probably can be made the most accurate. The sensibility of the levels should correspond with that of the leveling screws; that is, a small motion of the screw should produce a visible motion of the bubble of the level.

The water-level devices commonly used are (*a*) an automatic overflow; (*b*) sight box, which is simply an extension of the meter casing; (*c*) a gauge glass. The glass front of the sight box has a reference mark to which the water level is adjusted. The gauge glass has either a reference mark etched on it or some form of pointer. The latter has the advantage (or disadvantage) of being adjustable. A device used on one meter tested, consisting of two knife edges located one on each side of the gauge glass, proved very satisfactory. Experiments showed that there was little choice between the sight box and the gauge glass as far as reproducibility of water level was concerned, but the automatic overflow was decidedly inferior to either.

Briefly, the mode of action of wet meters is as follows:

The cylindrical measuring drum, rotating on a horizontal axis, is divided into four specially-shaped measuring compartments by

suitable partition walls, with nearly radial outlets on the front face and similar inlets on the back face of the drum. (See Fig. 4.) The drum is immersed in water to a depth of nearly two-thirds its diameter. Gas is admitted into the inlet chamber, which forms a fifth compartment at the rear of the drum, as shown in Fig. 5.

The measuring compartments are so shaped that the two nearly radial openings of a compartment in the back and front face of the drum, respectively, are at an angle of about 160°. The water level must be sufficiently high to seal off the opening in the inlet chamber through which the inlet tube and the shaft of the drum pass and to momentarily seal off both openings of the measuring compartment at the highest point of its revolution. The nearly radial openings in the front face of the drum are shown in Fig. 4. The shaded areas in this figure show the shape of one compartment. The mode of operation may be understood by following one compartment through a complete revolution. Starting with the compartment at its lowest point, both openings are under water and the compartment is filled with water. As the drum revolves, the opening at the rear passes out of the water and the gas enters, the water running out at the front opening. As the drum continues to turn, the compartment continues to fill with gas until it comes nearly to the top position. However, before the opening at the front emerges from the water the one at the back is closed by the water, thereby sealing off momentarily a certain volume of gas. As the drum continues to revolve the opening at the front emerges from the water and the gas escapes, being displaced by water entering at the back opening, until the compartment is again entirely submerged. It will be seen from the above description that in the operation of the meter both the gas and the water are caused to pass through the drum from back to front. Each compartment during each revolution delivers the amount of gas it contains at the instant it is sealed off. This amount will evidently depend upon the water level. The motive power is furnished by the difference of pressure of the gas on the two sides of the inclined partitions in the drum.

3. PREPARATION OF THE METER FOR USE

After filling the meter with water approximately to the gage mark, the meter was run for some time until the water was satu-

Fig. 4.—*Measuring drum of laboratory gas meter, showing radial openings of compartments. The blackened areas indicate the shape of one of the four measuring compartments*

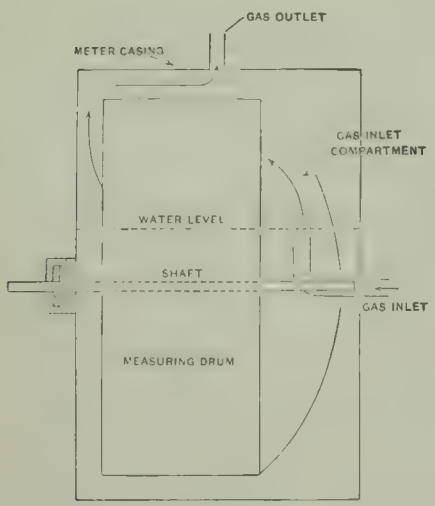


Fig 5.—*Section illustrating mode of operation of laboratory gas meter*

5. INVESTIGATION OF SOURCES OF ERROR

Experiments were made to determine the effects of errors in making the adjustments with such meters.

(a) **Method Used.**—For this purpose two meters were used in series. This method of comparing one meter with another can be used to determine to within 0.1 per cent the ratio of the volumes of gas delivered by the two meters, provided that care is taken to secure equality in the temperatures of the meters and of the room. The fact that one meter left undisturbed could be taken as constant to this degree of accuracy was established both by absolute calibrations and by determining the ratio to other meters also undisturbed.

The observations taken in comparing two meters in series are shown in Table 4. One observer gave a signal as the index of one meter passed the graduations noted in columns 1, 3, and 5, while the second observer noted the simultaneous readings of the second meter as recorded in columns 2, 4, and 6.

TABLE 4

Comparison of Meters No. 6312 and No. 246

[Temperature of meter No. 6312=80°0 F; temperature of meter No. 246=79°8; room temperature=80°6; rate=4.3 cubic feet per hour]

	First series		Second series		Third series	
	Meter No. 6312	Meter No. 246	Meter No. 6312	Meter No. 246	Meter No. 6312	Meter No. 246
	Cubic feet	Cubic feet	Cubic feet	Cubic feet	Cubic feet	Cubic feet
Initial readings	36.3800	11.4194	36.4800	11.5202	36.5800	11.6205
	.3900	290	.4900	293	.5900	300
	.4000	392	.5000	395	.6000	402
	.4100	483	.5100	486	.6100	494
	.4200	594	.5200	597	.6200	505
	36.4000	11.4391	36.5000	11.5395	36.6000	11.6401
Final readings	36.8900	11.9221	36.9900	12.0226	37.0800	12.1230
	.8900	318	.9900	322	.0900	327
	.9000	416	37.0000	420	.1000	424
	.9100	507	.0100	514	.1100	515
	.9200	618	.0200	623	.1200	625
	36.9000	11.9416	37.0000	12.0421	37.1000	12.1425
	36.4000	11.4391	36.5000	11.5395	36.6000	11.6401
Difference	.5000	.5025	.5000	.5026	.5000	.5024

Correction to No. 246 for difference in temperature=+0.0003, therefore 5.028 turns of No. 246=5.000 turns of No. 6312.

(b) **Leveling.**—If the meter is set up and the water level adjusted, then, tilting the meter in various directions up to 1° of arc (about 2 turns of leveling screw, 18 threads per inch) without changing the amount of water in the meter, produced no change exceeding 0.2 per cent in the calibration. However, readjusting the water level when the meter was tilted so that the gauge mark was raised or lowered through an angle of 1° with the horizontal caused a change in calibration of about 1.6 per cent.

(c) **Adjustment of Water Level.**—Investigation of several 0.1 cubic foot meters of different makes showed that a change in water level of 1 mm (0.04 inch) produced a change in calibration of from 0.5 to 0.8 per cent in the different meters, the meters delivering a smaller volume of gas per revolution when the water level was higher. It follows, therefore, that in order to reproduce the calibration to an accuracy of 0.1 per cent, the total error in adjusting the water content of the meter, whether the error be due to error in leveling or in adjusting water level, must not exceed the equivalent of 0.1 or 0.2 mm in the position of the water level in the gauge glass.

(d) **Temperature, Humidity, and Pressure.**—The actual quantity (i. e., mass) of gas delivered by the meter per revolution depends not only upon the volume of the compartments of the measuring drum and the position of the surface of the water, but also upon the temperature, humidity, and pressure of the gas in the measuring compartments. The meter must therefore be provided with a thermometer, so placed in the meter (preferably with the bulb in the water) as to indicate, as nearly as possible, the temperature of the gas in these compartments. While the temperature of the gas in the rotating drum can not be directly measured, this temperature will be approximately that of the water in the meter, provided that the temperature of the gas as it enters the meter does not differ too much from the temperature of the meter and that the meter is approximately at room temperature. As the water in the meter is well mixed by the movement of the drum, the temperature will be very nearly uniform throughout. An error of 1° F in the temperature of the gas will cause an error of approximately 0.3 per cent in the measurement of the gas.

Gas taken from a small holder with water seal is delivered to the meter practically saturated. To determine the effect of delivering relatively dry gas to the meter, the following experiment was made: Gas from the holder was passed through a copper coil immersed in ice to remove the moisture and then through two meters in series. In passing through the iced coil the saturation temperature of the gas was reduced to about 37° F. It was found that the calibration of the first meter, supplied with dried gas, did not change more than 0.1 per cent relative to the second meter from the calibration obtained when the first meter was supplied with saturated gas. The temperature of the meters was 75° F and the rate 7 cubic feet per hour. Humidity tests of the gas delivered by the first meter, when supplied with dried gas, showed the gas delivered to be saturated at the meter temperature. These experiments show that, at this rate, the gas was actually metered at the temperature indicated by the thermometer in the meter and that it had become practically saturated at that temperature.

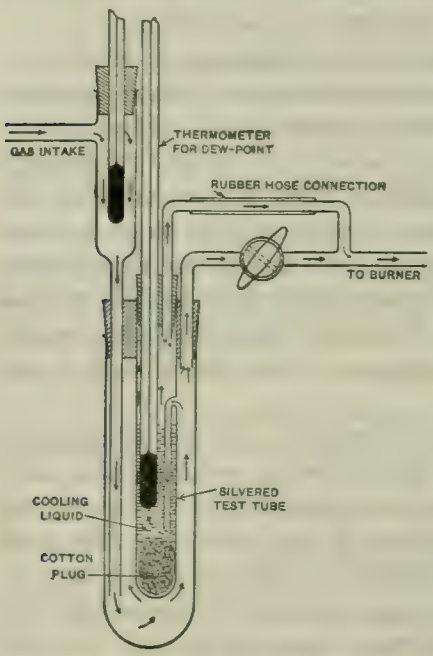


Fig. 6.—*Dew-point hygrometer*

The humidity of the gas was measured with a dew-point hygrometer, diagramatically shown in section in Fig. 6. The lowering of temperature of the inner silvered test tube was produced by evaporation of a volatile liquid and could be conveniently controlled by regulating the amount of gas passed through the stopcock. The dew point was directly read from the thermometer, the bulb of which was immersed in the liquid (ether or alcohol, depending on the lowering of temperature required) contained in the silvered test tube. The cotton plug in the bottom of the silvered test tube

prevented the cooling of this portion and the presence of dew was thus readily distinguishable by contrast between the bright surface below and the immediately adjacent surface above covered with a deposit of dew.

The effective pressure of the gas, when measured in the compartments of the meter drum, is the pressure in the inlet chamber and is practically equal to the pressure at the inlet of the meter. This pressure is usually a few inches of water above atmospheric pressure, corresponding to a few tenths of an inch of mercury, which must be added to the atmospheric pressure to find the pressure under which the gas was measured. If the inlet pressure is 2 inches of water, the corresponding correction due to this cause is about 0.5 per cent of the total pressure.

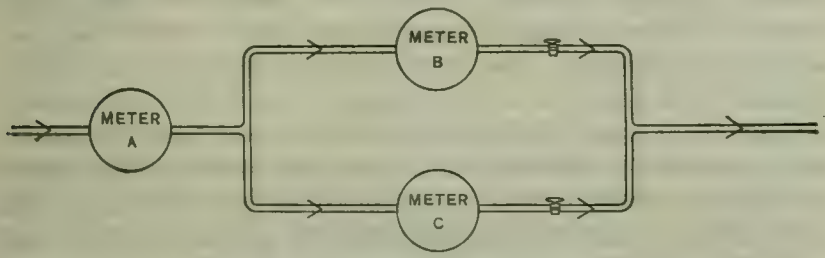


Fig. 7.—*Series-parallel arrangement of gas meters*

(e) Variation of Calibration with Rate.—The effect on the calibration of running these meters at different rates was tested in two ways—(*a*) by calibrations at different rates with a standard meter prover, and (*b*) by connecting three meters in a series-parallel combination, as shown in Fig. 7. The meter A, under test, was calibrated at a given rate, e. g., 5 cubic feet per hour, against B and against C, successively. Then A was calibrated at 10 cubic feet per hour against B and C running in parallel, each at 5 cubic feet per hour. B and C running at 10 cubic feet per hour were also tested against A at 10 cubic feet per hour. Since the effect of the given change of rate on A was known from the previous experiment, the effect of the change of rate on B and C was at once deducible. The conclusion from a series of such experiments was that the volume of gas delivered per revolution by these meters (one-tenth cubic foot), at rates between 2 and

10 cubic feet per hour, was constant to within about 0.1 per cent. This conclusion was further supported by the results of measurements of the drop in pressure through such meters. These measurements showed that the total drop was less than 0.1 inch of water and that the increase in the pressure drop, at rates between 2 cubic feet and 10 cubic feet per hour, was less than 0.01 inch of water; the consequent change in the water level must have been still smaller. Experiments with the meter prover showed that the meters delivered more gas per revolution at the higher rates—about 0.5 per cent more at 20 cubic feet and about 1 per cent more at 30 cubic feet per hour.

(f) **Reproducibility of the Calibration.**—To determine the reproducibility of the calibration the meter under investigation was emptied, refilled, releveled, water level readjusted, and recalibrated a number of times by comparison with a meter that had been left undisturbed. Such experiments on a number of meters, provided with sight box or gauge glass for water level adjustment, showed an average deviation of 0.1 per cent from the mean, with a maximum difference of 0.4 per cent between the highest and lowest calibrations for a series of six or more refillings. The order of reproducibility may therefore be put at about 0.2 per cent, although the error may evidently attain nearly 0.5 per cent. With an Elster internal-overflow meter differences in calibration, for different fillings with water, as great as 1 per cent were obtained. As the water level is not visible in this type of meter, the water level may vary considerably without the knowledge of the observer.

As an illustration of the behavior of a meter under working conditions there are given in Table 5 all the results of absolute calibrations of meter No. 6312, illustrated in Fig. 3, and which were made during a period of nearly two years. The meter was provided with a small plumb bob for leveling and the water level was adjusted to a mark on the glass of the sight box. Each calibration corresponds to a single adjustment of water level and is the mean of several calibrations by the aspirator bottle method. (See p. 35.) The variations among the calibrations made on different days but corresponding to a single adjustment of water level are nearly as great as among the tabulated mean values

corresponding to different adjustments of the water level, indicating that the variations are to some extent to be attributed to errors in the absolute calibrations.

TABLE 5

Absolute Calibrations of Meter, B. S. No. 6312

Date of calibration	Volume delivered per turn	Calibrated with—
	Cubic feet.	
November 6, 1911	0.1007	Illuminating gas.
October 5, 1912	.1003	Do.
October 8, 1912	.1004	Do.
June 17 to June 24, 1913	.1005	Natural gas.
July 21 to August 7, 1913	.1007	Illuminating gas.
August 12, 1913	.1009	Hydrogen.
Mean	.1006	

Experiments were also made on the method of adjusting the water level by filling the meter with water to a constant total weight. For this purpose two meters were connected in series, one meter being mounted on the pan of a balance. Intercomparisons of the two meters were made by the method illustrated by Table 4. From a series of eight experiments it was found that the calibration of the weighed meter, which was emptied and refilled before each intercomparison, could be reproduced to within 0.1 per cent, the maximum difference between any calibrations being less than 0.2 per cent. This method of adjusting the water level may sometimes be of use in permanent laboratory installations. If this method is used, the outer casing of the meter should be sufficiently rigid to withstand deformation. For large variations in temperature a correction would also be necessary (of the order of 1 part in 10 000 per 1° F) for change in water level due to change in temperature. The principal value of these experiments, however, consists in showing that reproducible calibrations may be attained if the water level adjustment is correctly made.

(g) **Fractional Revolutions.**—In the instructions for use accompanying some meters the use of fractional revolutions is specified.

This procedure is not to be recommended, as it may lead to very significant errors. For example, a test of one of these meters, the motion of the index of which over the scale was very regular, gave the results shown in Table 6.

TABLE 6 [8]

Volumes of Gas Delivered in Fractional Revolutions of Meter

Fractional revolution	Volumes of gas delivered	Volume delivered divided by 2820
	cc	
0.250	732	0.260
.333	972	.345
.500	1474	.523
.667	1924	.682
.750	2156	.765
1.000	2820	1.000

[8] The method of calibration used in the experiments summarized in this table was the aspirator bottle method, described on p. 35.

It will be seen that the volume of gas delivered in the second half revolution was 8.7 per cent less than in the first half revolution, and the volume delivered in the last one-third revolution was 7.8 per cent less than in the first one-third revolution. The quarter revolutions show similar differences. These meters should therefore be calibrated and used for total revolutions, or, if fractional revolutions must be used, the particular portion of the scale used must be calibrated.

(h) **Effect of Resistance to Rotation.**—All the conclusions stated above as to the accuracy of these meters, reproducibility of calibration, and independence of rate are true only if the meter is not required to do an appreciable amount of work, either in overcoming friction in the bearings or in overcoming resistance in a recording or other mechanism. If the meter is required to do work, there will be a difference of water level on the inlet and outlet sides, on account of the difference in pressure necessary to overcome the resistance, and the capacity of the drum will be changed by the change in level due to this cause to the same extent as by an error in adjusting the water level. The importance, therefore, of having the drum rotate so easily that the drop in pressure through the meter remains sensibly constant is readily seen. A criterion

as to the proper working of the meter may be obtained by determining whether the calibration is independent of the rate (up to about 10 cubic feet per hour). Such a determination may readily be made by using the aspirator bottle method of calibration.

6. ABSOLUTE CALIBRATION

These meters may be calibrated (*a*) by comparison with a standard meter prover, (*b*) by measurement of the volume of water displaced from a suitable container by the gas passed through the meter, and (*c*) with a standard bottle of known capacity.

(a) **Meter Prover.**—The meter prover must itself be tested against some standard volume, such as a cubic-foot bottle. The accuracy then attainable with it is less than the accuracy attainable with the wet meter, because of the difficulty of determining the temperature of the gas in the prover. Calibration with the meter prover is more time consuming than the other methods of testing small wet meters, as several cubic feet of gas must be run through the meter to obtain a sufficient length of scale reading on the prover to permit reading the scale length with the required accuracy. The meter prover is generally used for testing service meters, and is not well adapted to the testing of laboratory meters.

(b) **Aspirator Bottle.**—A simple, accurate, and inexpensive equipment for calibrating laboratory meters by the displacement method, using an aspirator bottle, is shown in Fig. 8. The volume of gas drawn through the meter for a given number of revolutions of the index is calculated from the corresponding weight of water displaced from the bottle. Before measurements are made, the water in the bottle should be saturated with the gas by displacing the water with the gas and refilling the bottle with the same water, repeating the operation several times.

If the highest accuracy is sought and the corrections are to be reduced to a minimum, it is necessary that the temperature of the gas entering the meter, of the water in the meter and in the bottle, and of the room be the same. These conditions are usually not difficult of attainment, within the requisite limits, if the temperature of the room is fairly constant. The main advantages of this method are (*a*) the temperature of the gas in the bottle is determinable since the gas passes through a tube in the large mass

of water, the temperature of which is that of the bottle and given by a thermometer suspended therein, and (*b*) the meter can be calibrated for the conditions of use with the calorimeter, viz, for the amount of gas delivered between successive passages of the index of the meter through the zero position.

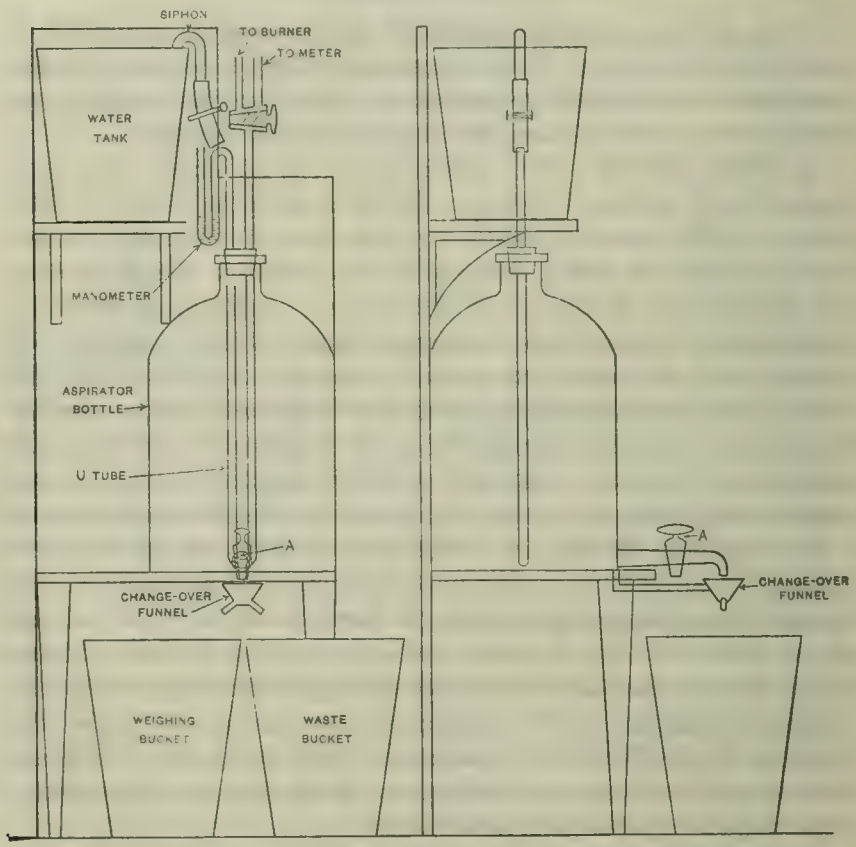


Fig. 8.—*Arrangement for calibrating gas meters by the aspirator bottle method*

The observations are made as follows: The apparatus is allowed to stand with the gas pressure on and with the lower stopcock, A, closed until it is evident that there are neither leaks nor absorption of gas by the water. With the change-over funnel set to allow the water to run to the waste bucket, the stopcock, A, is opened. As the index of the meter passes through the zero position the change-over funnel is shifted to allow the water to run into the

weighing bucket. After the index of the meter has made the desired number of revolutions, the funnel is shifted back just as the index passes through the zero position. The stopcock, A, is then closed. The volume of gas delivered is calculated from the weight of the water displaced. A sample observation showing the method of reduction is given in Table 7.

To refill the bottle with water the siphon tube is connected to the manometer, the three-way stopcock turned so as to permit the gas in the bottle to escape through a burner, the siphon started, and the gas lighted at the burner.

It is evidently possible by manipulating the stopcock, A, to use the method in the same way that the standard bottles (one-tenth cubic foot, etc.) are used, viz, by starting with the meter at rest and stopping it, after the desired number of revolutions, with the index in the initial position. The amount of gas delivered for any given fraction of a revolution may also be found.

TABLE 7

Calibration of Meter by Aspirator Bottle Method

Time	Start 2 : 54 : 38	End 2 : 59 : 17
Meter reading, cubic feet	46. 6000	46. 9000
Room temperature, degrees centigrade		25. 4
Meter temperature, degrees centigrade		25. 8
Bottle temperature, degrees centigrade		25. 2
Gas pressure at meter inlet, millimeters of water		36
Gas pressure in bottle, millimeters of water		28
Weight of water, grams		8481
Computation:		
Weight of water, grams		8481
Correction for buoyancy		+ 9
Correction for density of water		+25
Correction of difference of temperature of gas in meter and in bottle		+27
Correction for difference of pressure of gas in meter and in bottle		− 7
Volume of gas passed into meter, cubic centimeters		8535

1 revolution of index $=\frac{8535}{3}=2845$ cubic centimeters $=0.1005$ cubic feet.

A résumé of a large number of calibrations of different meters by this method has shown that the accuracy of a single determination is of the order of 0.2 per cent. The meters were found to measure the same volume of gas per revolution when tested as

ordinarily used with a calorimeter (i. e., for successive passages of the index of the meter through zero), or when tested with the index started from rest at zero and brought to rest at zero. The conclusion was that calibration by the latter method, which is that of the standardized bottle, introduced no error exceeding 0.1 per cent when the meter was used as it is with the calorimeter.

(c) **Standardized Bottles.**—Cubic foot or other standard volume bottles of suitable design may be used with considerable accuracy if the proper precautions are observed. For calibrating the gas meters used in calorimetry and photometry, small one-tenth or one-twelfth cubic foot bottles, of the type illustrated in Fig. 9, are often used. As the volume of the bottle may be determined from the mass of water necessary to fill it and the density of the water at the observed temperature, the error in this determination should be negligible. The change in the volume of the bottle itself due to change in temperature may in general be neglected. The temperature of the water in the standard bottle and in the meter under test should be as nearly as possible equal to the room temperature.

With the immersion type of bottle considerable error may be introduced due to the cooling of the bottle and the contained gas by evaporation from the outer wet surface of the bottle. As ordinarily used there may be a large error in the temperature assigned to the gas contained in bottles of this type, unless the air in the room is saturated.

The gas connections should always be tested for leaks before beginning the meter calibrations. If the meter and bottle are used with gas, the water with which the bottle is filled should preferably be saturated with the gas. If the bottle is filled with gas from a small holder with water seal, the gas will be practically saturated; if only partially saturated gas is used, it will become saturated in a short time if the inner walls of the bottle are wet.

In the ordinary method of use of standardized bottles a volume of gas, determined by the positions of upper and lower graduation marks on the bottle, is displaced through the gas meter. At the beginning and end of the displacement of gas from the bottle the pressure on the gas is only slightly in excess of atmospheric pres-

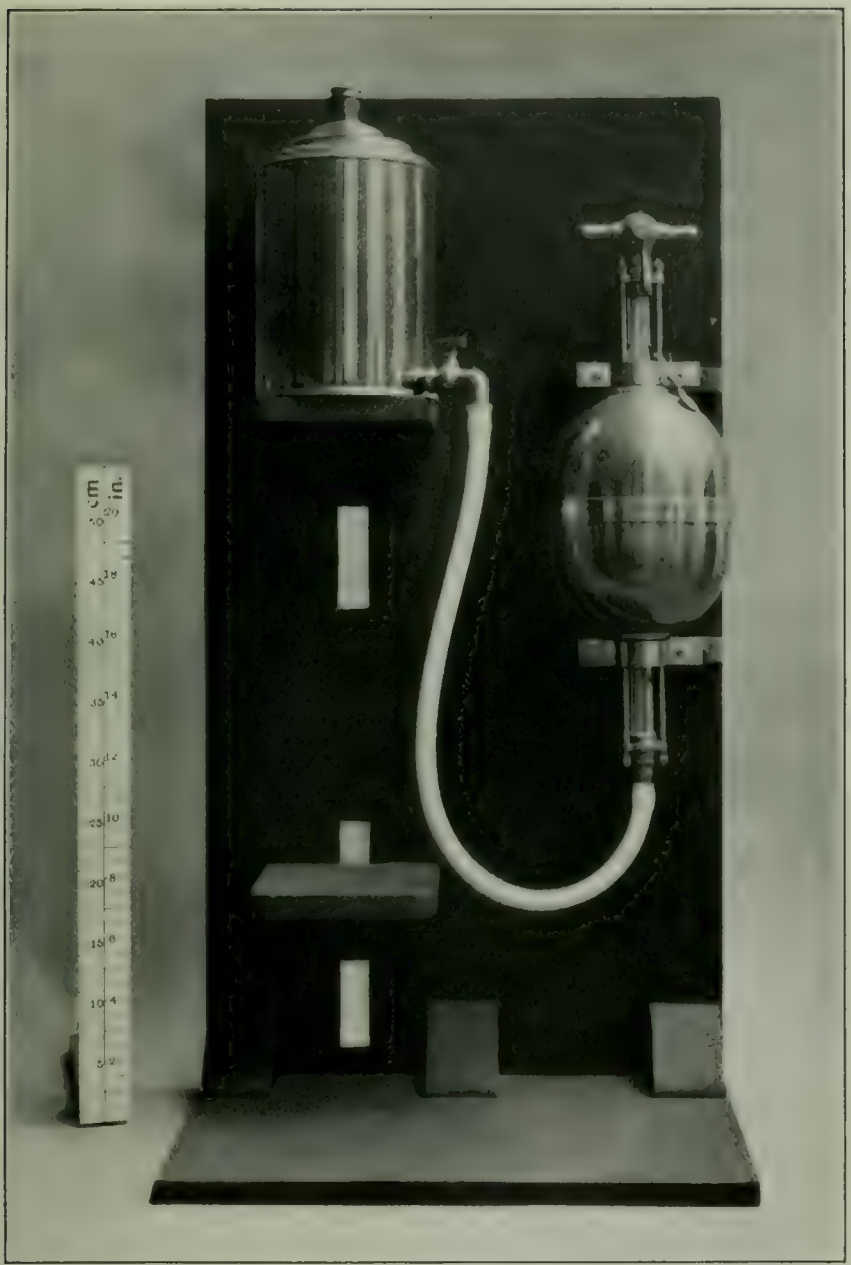


Fig. 9. *Standard volume bottle used for calibrating gas meters. Volume = 0.1 cubic foot*

sure, due to the static back pressure of the meter. The gas in the bottle is therefore measured practically at atmospheric pressure. When the meter is running the gas is under a somewhat higher pressure and is measured by the meter at this pressure; that is, its volume is smaller when measured in the meter. For a meter in good running order this excess of pressure, at the rates ordinarily used, is small enough to be neglected, being less than one-tenth of an inch of water.

A comparison of the aspirator bottle method of calibration, described on page 35, with the standardized bottle method was obtained by calibrating the same meter, first by the displacement method and then with a one-tenth cubic foot bottle. The standard bottle was used in two ways, first as above described and then by displacing the water in the bottle by gas which had been passed through the meter. The latter method has two advantages—(*a*) the temperature of the gas in the bottle may be more accurately determined since it is very nearly that of the water which has just been displaced, (*b*) there is less probability that the gas will be absorbed by the water in the bottle when the water is flowing out of the bottle than when it enters in a jet. Results obtained by the three methods are shown in Table 8.

TABLE 8

Comparison of Standard Bottle and Aspirator Bottle Methods of Calibration of Meters

(*a*) By aspirator-bottle method, one-tenth cubic foot=0.996_6 turn of meter.
(*b*) By one-tenth cubic foot bottle, displacing gas from bottle through meter, one-tenth cubic foot=0.996_0 turn of meter.
(*c*) By one-tenth cubic foot bottle, displacing water from bottle by gas from the meter, one-tenth cubic foot=0.997_3 turn of meter.

The results show that the methods are in satisfactory agreement.

7. SUMMARY OF METER TESTS

The meters used in these tests were: American Meter Co., one-tenth cubic foot; Elster, 3 liter; Sargent, one-tenth cubic foot; Alexander Wright & Co. (Ltd.), one-tenth cubic foot; John J. Griffin & Sons (Ltd.), one-twelfth cubic foot.

A large number of tests have shown that these meters, with the exception of the Elster with internal overflow, can be used to an accuracy of about 0.2 per cent when calibrated against a standard volume before use and, with due care in adjustment, may be used by different observers to reproduce an absolute calibration from time to time to within 0.5 per cent, provided the meter has suffered no mechanical injury, such as displacement of levels or of gage mark.

The calibration of the meters was found to be independent of the rate (to within 0.1 per cent) for rates of 2 to 10 cubic feet per hour. At 20 cubic feet per hour the meters were slightly slow (about 0.5 per cent).

The use of fractional turns may lead to significant errors, e. g., in the determination of the rate of flow in photometric tests. In one of the most smooth running meters examined the amount of gas delivered in the last one-third revolution was about 8 per cent less than in the first one-third revolution, with similar differences for other fractional turns. If fractional turns are used, the dial should be calibrated, e. g., by the aspirator bottle method.

It was found that the method of calibration by the standardized bottle, in which the meter is started from rest and again brought to rest, after a given volume of gas has passed through it, gave a calibration in agreement, to within 0.1 per cent, with a calibration made by determining the amount of gas delivered between successive passages of the meter index through the zero position.

The precautions to be observed in setting up the meter, such as leveling, adjusting of water level, saturating water in meter with the gas to be tested, the reduction of measured volumes to standard conditions of temperature, saturation and pressure, methods of absolute calibration of meters, and details of construction of meters have been considered in the preceding sections.

It will subsequently be seen that the accuracy with which the gas can be metered is of the same order as the accuracy with which some of the other factors which enter into a calorimetric measurement can be determined.

VII. FACTORS AFFECTING HEATING VALUE DETERMINATIONS WITH FLOW CALORIMETERS

The various factors which may influence the results of determinations of the heating values of gases by means of flow calorimeters may be somewhat arbitrarily divided into four groups, as follows:

(*a*) Those that affect the temperature measurements and the quantity of heat absorbed by the water, discussed under sections 1 to 7, inclusive.

(*b*) Those that affect the measurement of the amount of water run through the calorimeter during a test, discussed under sections 8 and 9.

(*c*) Those that affect the measurement of the volume of gas burned during a test, discussed under sections 10 to 12, inclusive.

(*d*) Certain factors depending upon the properties of the gas (particularly some illuminating gases) tested, discussed under sections 13 to 16, inclusive.

1. COMPLETENESS OF COMBUSTION

The question as to whether the combusion of the gas in the Bunsen burner of the calorimeter is complete could probably be most directly answered by a chemical analysis of the gas and of the products of combustion. While no such analyses have been attempted, considerable evidence has been obtained, all of which goes to show that the combustion of illuminating gas, natural gas, and hydrogen, in suitable burners, is complete within at least 0.2 or 0.3 per cent. Thus, in the experiments with natural gas burned in the Junkers calorimeter (see p. 104), different burners were used, the character of the flame was varied, etc., yet the heating values found for a given sample of gas were practically the same under all the different conditions. The experimental data summarized in Table 9 may be cited as typical of a large number of observations obtained during the progress of this investigation.

TABLE 9

Effect of Varying Character of Bunsen Flame

Character of Bunsen flame						Remarks
Normal		Partly luminous		Large excess of air; roaring		
Total	Net	Total	Net	Total	Net	
Btu	Btu	Btu	Btu	Btu	Btu	
685	622	.....	.....	685	622	Junkers calorimeter; illuminating gas.
753	682	753	679	751	[illegible]	Do.
683	628	683	629	[illegible]	629	Do.
.....	.....	638	.....	637	.....	Boys calorimeter; illuminating gas. Glass tube Bunsen burner.
999	902	.....	.....	998	901	Junkers calorimeter; natural gas.
.....	.....	.....	.....	[illegible]	901	Same, with Méker burner.

In Table 10 are summarized experiments made with the Boys calorimeter provided with a luminous flame burner which also indicate that, under ordinary conditions, the combustion is quite complete.

TABLE 10

Effect of Incomplete Combustion on Heating Value

Observed heating value, Btu	Gas rate, cubic feet per hour	Remarks
654	4.0	No evidence of incomplete combustion.
647	4.73	Dense smoke issued from calorimeter.
632	4.83	Very dense smoke.

It will be seen that the observed heating value had only been lowered by 1 per cent when dense smoke was issuing from the calorimeter. In several instances distinctly visible discharge of smoke from the calorimeter was noticed without any perceptible effect on the heating values found. With the Bunsen flame there is, however, a very evident drop in heating value as soon as incomplete combustion can be detected by the odor of the outlet products.

The effect of allowing the flame of the Bunsen burner to play against the inner wall of the combustion chamber of the Junkers calorimeter was tried and was found to cause no change in the

observed heating value. It did, however, result in increasing the irregularities in the readings of the outlet-water thermometer of the calorimeter.

That the combustion in the Bunsen burner must be very nearly complete would also seem to be indicated by the results of determinations of the heating value of a gas with very different ratios of volumes of air to gas (the so-called capacity-efficiency curves), such as are illustrated in Fig. 14, in which experiments the value of the ratio was varied from 20/1 to 7/1, and yet, under these very different conditions of air supply, the heating values found were the same.

Further corroborative evidence that the combustion is complete is furnished by the excellent agreement of the heating values found for natural gas and for hydrogen using the flow calorimeters, with the values found in calorimeters of the Berthelot bomb type, in which most perfect conditions for complete combustion are realized.

2. TEMPERATURE MEASUREMENTS

The inlet and outlet water thermometers should be graduated to 0°.1 C or to 0°.1 or 0°.2 F. For convenience in reading and to avoid errors of parallax, these thermometers should be provided with suitable reading glasses conveniently movable along the stem of the thermometer. If the thermometers are of the stem type and are read with the unaided eye, errors of parallax may be avoided by adjusting the line of sight so that the graduations near the mercury meniscus are seen superimposed on their images reflected from the mercury thread. If the thermometers are of the inclosed scale type, the line of sight should be so adjusted that the portion of the graduation, near the mercury meniscus, seen through the fine capillary stem, is in the same straight line with the ends of the graduation seen on either side of the capillary stem.

The thermometers should be so placed that they assume the true mean temperature of the water entering and leaving the calorimeter; that is, their bulbs must be in the flowing stream of water in such a position that the formation of a dead space around the bulb is not possible. The tops of the bulbs should be sufficiently far (0.5 inch) below the lower surface of the stoppers in which the thermometers are mounted so that the effect of heat

conduction to the bulbs is negligible. On account of the small bulb space available in the inlet and outlet tubes of most calorimeters this condition can not always be realized unless the bulb is made short.

The bulb of the inlet-water thermometer is subject to a slightly higher external pressure than is the bulb of the outlet-water thermometer. In extreme cases an error of 0°.02 F may be introduced due to this cause. Such error may, however, be eliminated by determining the differential correction (see p. 48) with the thermometers mounted in the calorimeter.

It is important that the heated water be thoroughly mixed before reaching the bulb of the outlet-water thermometer. This is usually accomplished by interposing in the path of the water a series of baffle plates. Other methods are also used, some of which are not so effective as might be desired. Thus, the apparent efficiency of one calorimeter tested was somewhat in excess of 100 per cent, which was traced to the fact that the outlet-water thermometer, in the position in which it was used, indicated a temperature higher than the true mean temperature of the effluent water, due to imperfect mixing in the efflux tube.

Sudden and relatively large variations in the readings of the outlet-water thermometer may be due to the accumulation of air bubbles and the formation of an air pocket in the calorimeter, which cause variations in the flow of water, or to air currents in the neighborhood of the calorimeter, which cause variations in the rate of heat transfer to the water. Variations in the rate of water flow, due to trapping of air in the water spaces, can be minimized if all the air is displaced by water, on starting the calorimeter. For example, in the Junkers and similar calorimeters there is little probability that the air will accumulate in the main part of the calorimeter, where the direction of flow is upward. However, at certain rates of water flow air will be trapped in the vertical pipe from the inlet weir. If this air is removed by closing and opening the inlet valve several times, the flow of water becomes and remains quite regular. In some calorimeters air may accumulate under a horizontal or sloping surface, and with such calorimeters there is always more or less irregularity of water flow, e. g., a Junkers calorimeter, new type, (see p. 118) showed this effect.

In other calorimeters, e. g., the Simmance-Abady, air may accumulate under the stopper supporting the inlet-water thermometer and, unless some device is provided to carry off this air, it is necessary to remove it by loosening the stopper from time to time. Variations due to drafts can be reduced in magnitude by shielding the calorimeter from drafts and by the observer avoiding sudden movements during the short time required for the temperature observations.

A sudden drop in the temperature of the inlet water will result in giving an observed heating value that is too high and a sudden rise a value that is too low. Observations in which the temperature of the inlet water varies by more than a few hundredths (0°.05 F) of a degree during the time of a single determination of the heating value should be rejected, unless the method of observation referred to below is used.

The method used by Immenkötter[9] of reading the inlet-water thermometer earlier than the outlet-water thermometer by the length of time required for the water to pass through the calorimeter largely eliminates errors due to variations in the inlet water temperature, and is therefore to be preferred, especially in the absence of thermostatic control of inlet water temperature.

The method of Immenkötter does not take into account the amount of heat involved in the change of the temperature of the metal parts of the calorimeter which occurs when there is a change in the inlet water temperature, and does not therefore completely eliminate the effects of changes in the inlet water temperature. The error, however, is not important, as may be seen from the following considerations. None of the calorimeters weigh much more than 20 pounds. If all of this weight were due to metal in contact with the circulating water, the water equivalent of the calorimeter would be about 2 pounds. In burning 0.2 cubic foot of a 600 Btu gas in a test, the quantity of heat measured is 120 Btu. If the temperature of the inlet water changed 0°.1 F during the test, the error introduced due to the heat capacity of the calorimeter would be 0.2 Btu in 120 Btu, or about 0.2 per cent. If the method of Immenkötter had not been used, the error would have been dependent upon a number of factors, such as water capacity of calorim-

[9] See footnote 5, p. 16.

eter, rate of flow, heat capacity of metal parts, etc., but the error would probably not in any case have been less than that estimated above.

Stem Correction.—Another possible source of error in the temperature measurements arises from the failure to take into account the emergent stem corrections of the thermometers. When the mercury in the stem of a thermometer is at a lower (or higher) temperature than the mercury in the bulb, the thermometer will read too low (or too high), provided it is graduated to read correctly or that it is tested when totally immersed; that is, when the bulb and stem, at least to the mercury meniscus, are at the same temperature. The correction for emergent stem may be computed from the formula:

$$\text{Stem correction} = K \times n\,(T° - t°).$$

K = factor for relative expansion of mercury in glass; 0.00015 to 0.00016 for centigrade thermometers, 0.000083 to 0.000089 for Fahrenheit thermometers, at ordinary temperatures, depending upon the glass of which the stem is made.

n = number of degrees emergent from the bath.

T = Temperature of the bath.

t = mean temperature of the emergent stem.

If the water enters the calorimeter very nearly at room temperature, the stem correction for the thermometer used to measure the temperature of the entering water will be entirely negligible. If the water leaves the calorimeter 18° F (10° C) above room temperature, the emergent stem of the thermometer used to measure this temperature will be at a lower temperature than the immersed portion, and this thermometer will therefore read too low by an amount depending upon the number of degrees emergent and upon the number of degrees by which the mean temperature of the emergent stem differs from the temperature of the bulb.

As an example, approximating conditions often found in practice, assume that the room temperature is 68° F, the observed temperature of the water as it enters the calorimeter is 68°.00 F, and as it leaves the calorimeter 86°.00 F, and that a length of stem of the outlet-water thermometer corresponding to 54° F is emer-

gent from the calorimeter. Under these conditions the average temperature of the emergent stem will be about 70° F. Then

$$\text{Stem correction} = 0.000085 \times 54 \times (86° - 70°) = 0°.07 \text{ F.}$$

Hence the true temperature of the effluent water is 86°.07 F. The stem correction for the inlet-water thermometer, under the above conditions, is obviously zero. If the temperature of the inlet water differs sufficiently (2° or 3°) from the temperature of the room, the stem correction should be computed for the inlet-water thermometer in the same way as shown above. Neglecting the stem correction in the above example would cause an error of 0°.07 in 18° F, or about 1 part in 250; that is, 0.4 per cent in the resulting heating value. Under extreme conditions, with high room temperatures, the error due to neglecting stem corrections may attain 0.5 per cent. For thermometers made in accordance with the Bureau's specifications the error due to neglecting stem corrections would not exceed 0.4 per cent of the temperature interval and would generally be about 0.2 per cent.

Accuracy.—If the inlet and outlet water thermometers are used without being standardized, errors of 0°.3 or 0°.4 F in the usual working interval of 15° to 20° F are possible, which correspond to a quantity of the order of 2 per cent in the resulting heating value (i. e., 12 Btu in 600 Btu). With a careful standardization of the thermometers this possible source of error may be reduced to about 0°.04 F, or 0.2 per cent (i. e., 1 Btu in 600 Btu).

Auxiliary Temperature Measurements.—The effect of errors in the gas meter thermometer is considered on page 29, where it is seen that an error of 1° F in the measurement of the temperature of the gas in the meter causes an error of about 0.3 per cent in the resulting heating value.

An error of 1° F in the measurement of the temperature of the escaping products of combustion will cause an error in the estimation of the sensible heat carried off by the products which is less than 0.1 per cent of the heating value of an ordinary illuminating gas.

The measurement of room temperature does not require a high-grade thermometer so much as it does the proper use of the thermometer to give a true indication of the average temperature of the air in the neighborhood of the calorimeter and gas meter.

The temperature of the room is sometimes read from a thermometer at some distance from the calorimeter, and so placed that its temperature may be influenced by surrounding objects, e. g., steam pipes, flues, windows, walls, etc., under which conditions the indications of the thermometer may give a very erroneous idea of the average temperature of the calorimeter surroundings. In the present investigation room temperatures were measured by the dry-bulb readings of the Assmann psychrometer, placed near the calorimeter. In this instrument the air is circulated past the dry bulb of the thermometer, which is so mounted as to protect the bulb very effectively from the effects of radiation from surrounding objects, and conduction from the metallic parts of the instrument. The position of the psychrometer must of course be judiciously selected so that the air is not drawn over heated or cooled surfaces. An error of 1° F in the estimation of the room temperature would not lead to an error in the resulting heating value exceeding 0.1 per cent, except under unusual conditions.

All of the thermometers used with the calorimeters tested in this investigation were carefully compared with two standard thermometers so that their indications were at once reducible to standard gas-scale temperatures.

Specifications for Calorimetric Thermometers.—Complete specifications in accordance with which calorimetric thermometers have been made up by a number of thermometer makers, and which have proved most satisfactory in every way, will be published in a special Bureau circular. While it is true that, for most purposes, it is desirable to have the ice point on the scale of a thermometer, on account of the convenience with which any secular changes in the thermometer can be measured and allowed for by a determination of the ice point from time to time, this is not necessary for differential measurements, as in calorimetry. If the thermometers have once been standardized, any changes in their corrections relative to one another can easily be determined by intercomparing them at room temperature in a well-stirred pail of water, or while in position in the calorimeter with no gas burning and with the inlet water at room temperature.

If the observed readings of each thermometer are then corrected by the corrections given in the certificates, the difference in these

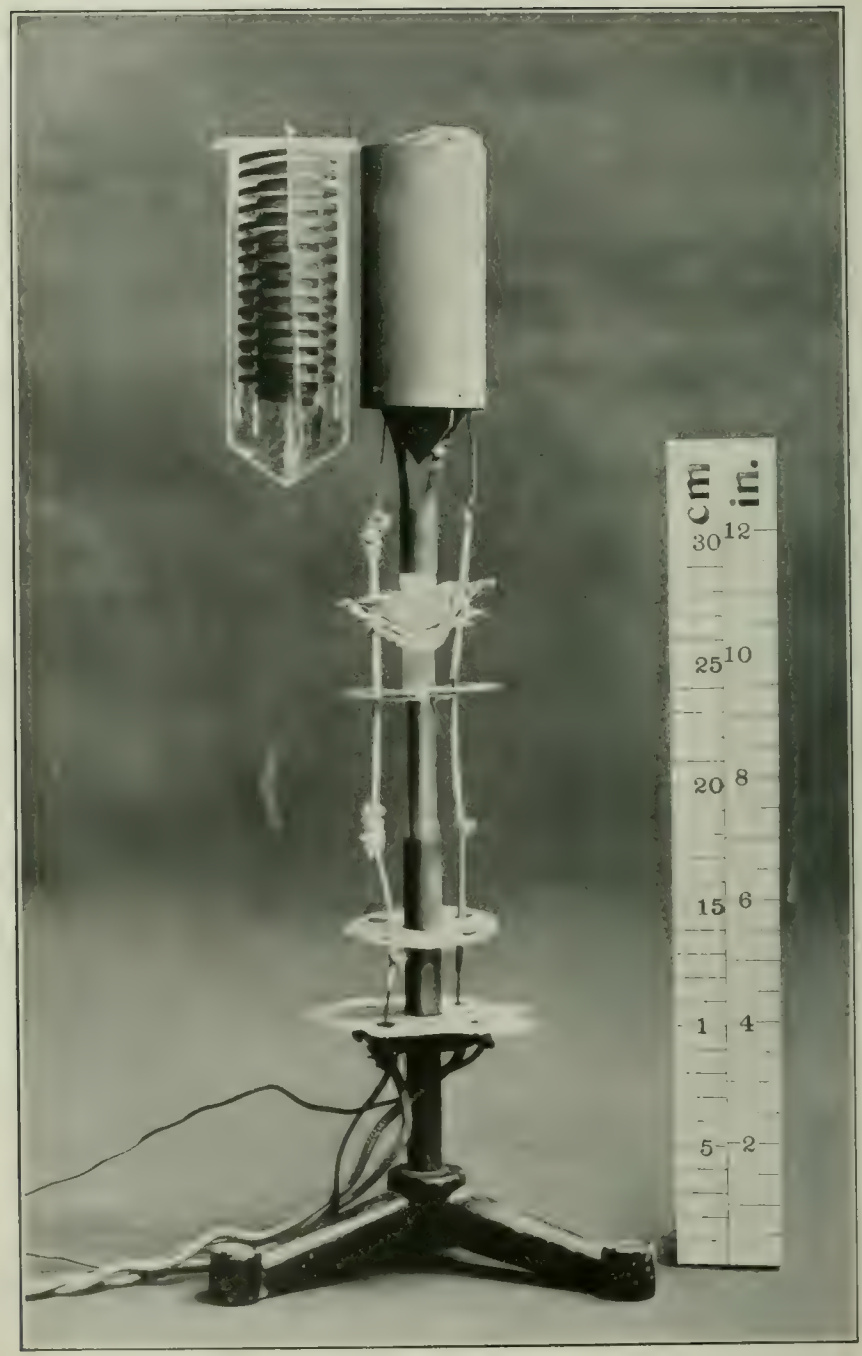


Fig. 10.—*Electric heating coil*

corrected readings is the relative change (at all points of the scale) which has occurred since the thermometers were certified. In the subsequent use of the thermometers, a so-called differential correction, to allow for this relative change, should be applied to the readings of one of the thermometers (preferably the outlet-water thermometer) in addition to the corrections given in the certificates.

3. HEAT LOSSES FROM CALORIMETER

Owing to various heat interchanges between the calorimeter and the surroundings, the observed heating value will, in general, differ from the total heating value of a gas by an amount depending upon the conditions prevailing during the experiment as well as upon the efficiency of the calorimeter as an absorber of the heat set free in the combustion chamber.

(a) **Efficiency of Calorimeter.**—Some idea of the efficiency of the calorimeter as a heat absorber may be obtained by supplying heat electrically within the combustion chamber at a known rate and observing how much of this heat is recovered in the stream of water flowing through the calorimeter. For this purpose the electric heating coil, illustrated in Fig. 10, was constructed. This coil consisted of a number of turns of nichrome ribbon, suitably insulated by mica, and provided with terminals to enable the potential difference between the proper points to be accurately measured. On the support for the coil was mounted a series of metal disks, as shown, to diminish the loss of heat through the bottom of the combustion chamber.

The expenditure of electric power in the coil was measured as follows: In series with the coil was connected a standard resistance (0.1 ohm), across the potential terminals of which the potential difference was measured by means of a potentiometer, the data so obtained serving for the calculation of the current through the heating coil. The other factor required, viz, the potential difference at the terminals of the heating coil, was determined by connecting the potential terminals of the coil to a 100:1 volt box, and then measuring the known fraction of the total potential difference by means of the potentiometer. The accuracy of calibration of the electrical apparatus was such that the measurements thus made should be reliable to at least 1 part in 10 000.

After the heating coil was placed in position within the calorimeter the electric current was regulated to give the desired expenditure of power in the heating coil, the flow of water through the calorimeter being so adjusted as to give the desired difference in reading between inlet and outlet water thermometers. The current was supplied by a 120-volt storage battery and remained very constant. The heating current was left on the coil for at least 45 minutes before beginning observations, to allow the attainment of equlibrium conditions. This was necessary on account of the considerable heat capacity of the coil supports.

During a known interval of time, usually three minutes, frequent readings were taken of the inlet and outlet temperatures of the water, the temperature of the air escaping through the products outlet, the current through the heating coil, and the potential difference at its terminals. The data summarized in Table 11 for one efficiency determination will serve to illustrate the method:

TABLE 11

Determination of Efficiency of Junkers Calorimeter No. 1209 by Electric Method

Mean inlet temperature of water, degrees centigrade	18.35
Mean outlet temperature of water, degrees centigrade	24.98
Mean temperature of escaping air, degrees centigrade	19.0
Mean temperature of room, degrees centigrade	18.0
Mean heating current through coil, amperes	10.839
Mean p. d. at terminals of coil, volts	47.86
Mass of water delivered in 180 seconds, grams	3360

The heat recovered in the water was

$3360\times(24.98-18.35)=22\,277$ calories (22° cals.)

$=22\,244$ calories (15°)

The energy expended in the heating coil was

$10.839\times47.86\times180.0=93\,376$ joules

$=22\,301$ calories (15°)

The efficiency of the calorimeter *as used*, when efficiency is understood to mean the ratio of the energy recovered in the water to the energy expended in the heating coil, is therefore

$$\frac{22\,244}{22\,301}=99.7 \text{ per cent}$$

The results of a number of such determinations on different calorimeters, made under different conditions as to rate of supply of electric energy to the coil and of flow of water through the calorimeter, are summarized in Table 12.

TABLE 12

Efficiencies of Flow Calorimeters by Electric Method

Date	Calorimeter	Determinations	Efficiency
			Per cent
November, 1910	Junkers No. 1209	15	99.8
July, 1912	do	4	100.0
September, 1911	Simmance-Abady, American type	3	98.9
October, 1911	Sargent	4	99.6
November, 1911	Simmance-Abady, English type	12	99.1–100.4
	do	7	99.7–100.3
	do	10	99.7
July, 1912	Hinman	10	99.9
October, 1911	Boys	2	96.0

As the accuracy of these tests is of the order of 0.2 or 0.3 per cent, it may be said that the efficiencies of the Junkers, Hinman, Sargent, and Simmance-Abady (English type) calorimeters as heat absorbers are practically the same, all being in excess of 99.6 per cent.

The low value found for the efficiency of the American type of Simmance-Abady calorimeter is undoubtedly due to the heat conducted away by the heavy metal tube which extends through the center of the calorimeter, and which is not in contact with the circulating water but is in good thermal communication with the heavy metal base of the calorimeter. The outer cylinder of the heating coil was very close to this tube, so that the efficiency may have been lower than with a Bunsen flame in the combustion chamber. In the Boys calorimeter the combustion chamber is so short that the heat losses from the base were very great with the heating coil used, which was not adapted to this calorimeter. The low efficiency found for this calorimeter, however, is in part corroborated by the low values obtained for the total heating value of illuminating gas.

The varying results obtained with the Simmance-Abady calorimeter are due to the fact that the perforated cone around the bulb of the outlet-water thermometer did not mix the water sufficiently to insure that the thermometer should indicate the true mean temperature of the effluent stream. When a suitable mixing device was substituted for the perforated cone supplied with the instru-

ment, more satisfactory results were obtained. The first series given in the table corresponds to determinations with the cone, the second series to determinations with no mixing device, and the third series to determinations with a baffle-plate mixer. Apparent efficiencies appreciably in excess of 100 per cent are due to errors in the indications of the outlet-water thermometer.

The meaning of such tests of the efficiency of a calorimeter has been often misinterpreted. As stated in the beginning of this section, such tests give an indication as to the proper design of the calorimeter (e. g., the sufficiency of heat-absorbing surface, of mixing of outlet water, etc.). However, when gas is burned in the calorimeter, the observed heating value is not the same proportion of the total heating value as is indicated by the efficiency as determined by the electric method; or, in other words, if the efficiency of a calorimeter had been found by the electric method to be 99.8 per cent, the observed heating values obtained with the calorimeter would not necessarily be equal to but might be very appreciably different from 99.8 per cent of the total heating value of the gas tested. The net heating value (uncorrected for heat losses) would, however, be approximately the same proportion of the true net heating value as is indicated by the efficiency determined electrically.

(b) **Surface Losses.**—The heat lost to the surroundings from the external surface of the calorimeter will depend upon the average excess of temperature of its surface above that of the surroundings, to some extent upon the physical condition of the surface as to polish, etc., and upon the condition of the air in contact with the surface, i. e., whether at rest or in motion. The heat loss from the surface may be considered under two heads, the loss due to the average excess of temperature of the surface of the calorimeter above the temperature of the inlet water, and a further loss (or gain) of heat due to the inlet water being above (or below) room temperature.

With gas burning in the combustion chamber of Junkers calorimeter No. 1209, the flow of water adjusted to give a 10° C rise in temperature, and the calorimeter shielded from drafts as usual, the temperature of the surface was measured at a number of points by means of a "surface thermocouple." This couple consisted of a fine constantan wire, the ends of which were soldered to

thin copper disks. A fine copper wire was also soldered to each of the copper disks, these wires serving as leads to a reversing switch which was connected to a galvanometer. One of the copper disks was mounted against the inlet water pipe, while the other was mounted against the part of the surface the temperature of which was to be measured. The disks were electrically insulated from the calorimeter by very thin sheets of mica. The disks, when pressed into intimate contact with the surfaces and loosely covered with cotton wool, must have assumed approximately the temperatures of the surfaces, and hence the electromotive force of the thermocouple was a direct measure of the excess of temperature of the one junction above that of the inlet water.

The thermocouple was calibrated by mounting one junction against the inlet water pipe and the other against the side of the outlet wier and observing the resulting galvanometer deflection. The temperature of the water in the inlet pipe and in the outlet wier was measured with thermometers. This method of calibration reduced the error due to the thermojunctions not being exactly at the temperatures of the surfaces with which they were in contact.

The average temperature of the various parts of the surface of the calorimeter was found to be higher than that of the inlet water by the amounts stated below:

The small cylindrical portion at the top (effective area 125 cm²) was 5°.5 C warmer than the inlet water.

The upper conical surface (area 180 cm²) was 4° C warmer than the inlet water.

The surface of the cylindrical body of the calorimeter (area 1450 cm²) was 0°.9 C warmer than the inlet water.

The surface of the lower cylindrical portion (area 328 cm²) was practically at the same temperature as the inlet water.

The 2100 cm² of the surface were therefore on the average 1°.3 C warmer than the inlet water, when the rise of temperature of the water flowing through the calorimeter was 10° C.

The rate of loss of heat from a polished nickeled surface, similar to that of the calorimeter, was determined by observing the rate of cooling of a nickel-plated closed can of known area and containing a known mass of water about 7° warmer than its surroundings.

These observations showed that the loss of heat was about 0.006 calorie per minute per square centimeter per 1° C difference in temperature. The rate of heat loss from the calorimeter, when the inlet water was at room temperature, was therefore $2100 \times 1.3 \times 0.006 = 16$ calories per minute. This corresponds to 0.064 Btu per minute for a temperature rise of 18° F of the water flowing through the calorimeter.

That this heat loss is comparatively unimportant may be seen from the following considerations: In a calorimetric measurement in which a gas of 600 Btu is burned at 7 cubic feet per hour, the rate of heat supply is about 70 Btu per minute. The loss of 0.064 Btu therefore amounts to a little less than 0.1 per cent. This heat loss, which is ordinarily called the "radiation loss," has been given an unwarranted importance in the literature of the subject, often being cited to account for large discrepancies found. In nonflow calorimeters of the usual types, where the total amount of heat measured is only 30 or 40 Btu in an experiment lasting 10 minutes or more, this loss is of far greater relative importance.

For calorimeters of similar construction (i. e., with the water passing through the calorimeter in but one direction, and having approximately the same area and a similar air jacket) the heat lost to the surroundings under the conditions discussed above will be approximately the same as for the Junkers calorimeter. For externally water-jacketed calorimeters, such as the Simmance-Abady, the loss will be less. This loss being so small for most flow calorimeters, it was not deemed of sufficient importance to warrant investigation for each calorimeter.

There will be further heat interchanges between the surface of the calorimeter and its surroundings if the temperature of the inlet water is above or below that of the room. The rate of this heat interchange was determined for a number of calorimeters by observing the change in temperature of water flowing through the calorimeter, with no gas burning, when the temperature of the inlet water was above, or below, room temperature by about 18° F. From the change in temperature of and the rate of flow of the water, this rate of heat interchange was directly computed. These rates of heat interchange for a number of calorimeters are given in Table 13.

TABLE 13

Rate of Heat Interchange Between Calorimeter and Surroundings, in Btu Per Minute per 1° F Difference Between Inlet Water and Room Temperatures

Calorimeter	Btu per minute per 1° F	Calorimeter	Btu per minute per 1° F
Junkers No. 1209, original type	0.022	Junkers No. 1443, new type	0.022
Junkers No. 876, original type	.024	Simmance-Abady, English type	.055
Hinman-Junkers No. 164	.034	Simmance-Abady, American type	.052
Sargent	.034	Boys	.034

If the surface loss of 0.006 calories per square centimeter per minute per 1° C difference of temperature is used to compute what the loss of heat from the Junkers (original type) calorimeter would be per 1° C difference between inlet-water temperature and room temperature, if the outer casing were removed, the loss is found to be about 10 calories per minute. (The effective area would be about 1700 cm^2 and $1700 \times 0.006 = 10$.) This loss is, however, precisely equal to the loss found per 1° C difference between inlet water temperature and room temperature for the calorimeter with air jacket; that is, the above data make it appear that the heat loss in still air is not decreased by the presence of the air jacket. The quantities of heat measured in these experiments were small, so that the above data were not determined with a very high degree of accuracy, and hence the conclusion from these data that the air jacket does not materially affect the amount of heat interchange between the calorimeter and the surroundings must be regarded as a first approximation. It is, however, probably true that the efficiency of the air jackets on these calorimeters has been overestimated. So far as is known to the authors no attempt has been made to verify experimentally the assumption that the air jackets materially reduce the heat losses from the calorimeters. However, it is probably true that the jackets do no harm, and they may be of advantage in reducing fluctuations in the amount of heat loss due to varying air currents.

In the Hinman-Junkers and Sargent calorimeters there is a long inlet water tube between the inlet-water thermometer and

the calorimeter for the purpose of bringing the inlet and outlet thermometers on the same level, a form of construction which probably accounts for the fact that the constant found is larger than for the Junkers calorimeter.

The effect of this heat interchange on a calorimetric measurement may be seen from the following considerations: Suppose the Sargent calorimeter were operated with the inlet water 5° F colder than the room, and a 600 Btu gas were being burned at 7 cubic feet per hour; the heat gained from the surroundings is $5 \times 0.034 = 0.17$ Btu per minute, which is 0.24 per cent of the heat (70 Btu per minute) furnished by the combustion of the gas. This, however, is not the only error introduced by operating the calorimeter with the inlet water below room temperature. Other errors due to this cause are considered on page 78.

It is obvious that, for a given calorimeter, the temperature of the inlet water may be so chosen that the sum of all *surface losses* (plus and minus) will be zero. For example, if the Junkers calorimeter No. 1209 were operated with the temperature of the inlet water 3° F below room temperature (no gas burning), it would gain $3 \times 0.022 = 0.066$ Btu per minute. Then, if gas is burned in the calorimeter so as to produce a rise of temperature of 18° F in the water passing through, there would be a rise in the average temperature of the surface sufficient to superimpose a loss of 0.064 Btu per minute, which almost exactly neutralizes the gain due to the inlet water being below room temperature. This result may also be stated as follows: If I be the temperature of the inlet water and O that of the outlet water, the calorimeter will interchange heat with its surroundings at the rate at which it would interchange heat if water at a temperature $I + \frac{1}{6}(O - I)$ were flowing through the calorimeter with no gas burning (instead of $I + \frac{1}{2}(O - I)$ as has been assumed by some authors).

While the losses from the surface of the calorimeter may be eliminated by the method of compensation described above, the procedure is not to be recommended for several reasons; (*a*) it is easier to maintain the inlet water at room temperature; (*b*) the tables of corrections for atmospheric humidity (see p. 77) would not be applicable and, since the compensation would differ for different calorimeters, separate tables of corrections for atmos-

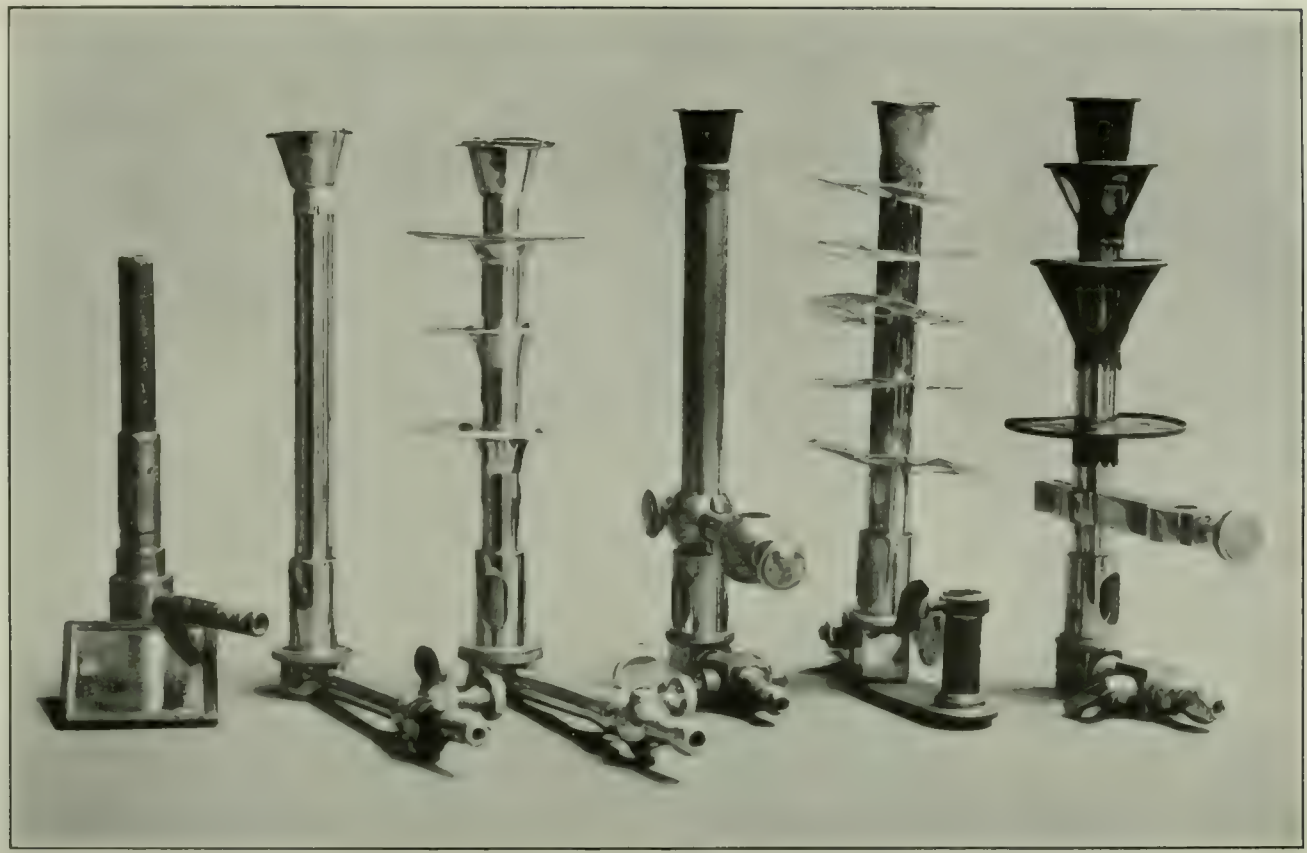


Fig. 11. *Types of burners and radiation shields*

pheric humidity would be necessary for each type of calorimeter; (*c*) for most of the calorimeters included in these tests the surface heat loss, when the inlet water is at room temperature, is so small that it is inadvisable to modify the method of operation in order to compensate for the loss. The method of operating with the inlet water at room temperature is therefore preferable.

(c) **Position of Burner in Calorimeter and Use of Radiation Shields on Burner.**—Merely holding the hand under the bottom of the calorimeter when the burner is lighted makes it evident that some heat is being lost from the calorimeter. The amount of this loss will evidently depend to some extent upon the position of the burner; that is, it will be larger if the burner is set low, and may be diminished by raising the burner. The loss may be further diminished by mounting on the stem of the burner several radiation shields which may be made of thin polished metal disks perforated to admit air freely to the flame. Fig. 11 shows several burners equipped with various forms of radiation shields.

Position of Burner.—With most of the calorimeters tested, it was found that the burners were so mounted that they could not be inserted far enough into the combustion chamber. Thus, in the Junkers calorimeter (original type), while the heat loss was not sensibly diminished by raising the burner, it was found that even with the burner set as high as possible with the mounting furnished, the products of combustion were reheated several degrees Fahrenheit in the lower part of the calorimeter. When the burner support was modified, and the burner was raised about 1.5 inches higher and was provided with radiation shields, the products escaped from the calorimeter at a temperature not more than 0.5° F above that of the inlet water. No advantage resulted from further raising the burner. The reheating of the products has led many observers to underestimate the efficiency of the heat-absorbing system of the calorimeter and has also been the cause of some peculiar operating directions. As soon as the reheating of the products is eliminated it is at once evident why the escaping products must be saturated at or a little above the temperature of the inlet water, as was found by Immenkötter as the result of an extended investigation.

The effect that the position of burner may have on the resulting heating values is shown by the results given in Table 14 and which were found with Simmance-Abady calorimeters of the English and American types and with a Junkers calorimeter.

TABLE 14

Effect of Position of Burner on Heating Values

Date	Calorimeter	Position of burner	Heating values in Btu (without radiation shields)	
			Observed	Net
November 4, 1911	S.-A. English type.	Mounted on stand as furnished	655	
	do	Burner raised 3 inches	661	
November 10, 1911	S.-A. American type.	Burner mounted as furnished	695	639
	do	Burner raised 3 inches	706	646
May 22, 1913	Junkers No. 1209	Burner set as high as possible with mounting furnished.	647	598
	do	Burner set 1½ inches higher	648	599

It will be seen that the heating values found with the Simmance-Abady calorimeters were raised 1 per cent or more by raising the burner 3 inches.

Radiation Shields on Burner.—The use of radiation shields on the burner will raise the observed heating value by diminishing the sensible heaf lost through the bottom of the calorimeter. The shields may also exert a slight influence in the direction of raising the observed heating values by returning to the inflowing current of air some of the heat that might otherwise be lost by conduction down the stem of the burner.

If a calorimeter were operated so that a considerable excess of air over that required for combustion was drawn through it, the addition of close-fitting shields with small openings might also raise the observed heating value by reducing the excess air supply, provided the air supply were still sufficient to insure complete combustion. The net heating value would not be affected, due to this cause. Such an effect, however, has not been observed with any of the shields used during the present series of experiments, the observed heating value being affected to practically the same extent as was the net value.

The results of a large number of experiments on the several calorimeters are summarized in Table 15. The experiments were made alternately with and without shields, all other conditions (except of course such change in air supply as was thereby caused) remaining the same in any one series of experiments. The table includes the results of some 150 determinations of heating values, and, with the exception discussed below, in no instance was the heating value with shields as low as without shields.

TABLE 15

Effect of Shields on Heat Losses

Date	Calorimeter and conditions of experiment	Gas rate, cubic feet per hour	Heating values, Btu		Increase due to shields, per cent
			Total	Net	
	Hinman-Junkers calorimeter No. 91:				
July 17, 1912	Without shields, damper open	12	670	616	0.7 in total
	With shields, damper open	12	675	620	0.6 in net
	Without shields, damper open	5.5	666	616	1.0 in total
	With shields, damper open	5.5	673	621	0.8 in net
July 18, 1912	Without shields, damper open	7	667	618	
	Heavy copper shields, damper open	7	671	621	0.6 in total
	Light aluminum shields, damper open	7	671	621	0.5 in net
	Without shields, damper open	7	667	618	
	Sargent calorimeter:				
Oct. 7, 1911	Without shields, damper open	4	676	.....	0.7 in total
	With aluminum shields, damper open	4	681	.....	
	Simmance-Abady calorimeter, English type (burner 3 inches higher than normal position):				
Nov. 7, 1911	Without shields, damper open	5	657	.....	0.6 in total
	With shields, damper open	5	661	.....	
	Simmance-Abady calorimeter, American type (burner 3 inches higher than normal position):				
Nov. 10, 1911	With shields, damper open	3	708	648	0.4 in total
	Without shields, damper open	3	708	646	0.4 in net
	With shields, damper open	3	709	649	
	Boys calorimeter:				
Sept. —, 1911	Without shields	4	644	.....	0.0 in total
	With 4 aluminum shields	4	643	.....	
	With 2 aluminum shields	4	645	.....	
	Junkers calorimeter No. 1209:				
Aug. 24, 1912	Without shields, burner very high, damper closed	7	701	644	0.6 in total
	With shields, burner very high, damper closed	7	705	649	0.5 in net

TABLE 15—Continued

Date	Calorimeter and conditions of experiment	Gas rate, cubic feet per hour	Heating values, Btu		Increase due to shields, per cent
			Total	Net	
	Junkers calorimeter No. 1209—Continued				
May 22, 1913	Without shields, burner very high, damper closed	7	657	.....	
	With shields, burner very high, damper closed	7	658	.....	
May 23, 1913	Without shields, burner highest position as furnished, damper closed	7	655	.....	0.2 in total
	With shields, burner highest position as furnished, damper closed	7	656	.....	
May 24, 1913	Without shields, burner as above, damper open	7	648	.....	
	With shields, burner as above, damper open	7	650	.....	
	Hinman-Junkers calorimeter No. 164:				
May 26, 1913	Without shields, burner highest position as furnished, damper closed	5.5	660	609	0.5 in total 0.5 in net
	With shields, burner highest position as furnished, damper closed	5.5	[illegible]	612	
May 27, 1913	Without shields, burner 1½ inches higher than above, damper closed	5.5	652	601	0.2 in total 0.0 in net
	With shields, burner 1½ inches higher than above, damper closed	5.5	653	601	
	Without shields, burner 3 inches lower than first position, damper closed	5.5	[illegible]	598	0.2 in total 0.2 in net
	With shields, burner 3 inches lower than first position, damper closed	5.5	649	599	

The effectiveness of the shields in reducing the heat loss is perhaps best shown by the curves, Fig. 14, for observed and net heating values obtained with the Hinman-Junkers calorimeter No. 91, operated at different rates of gas consumption, which show that the heating values obtained with shields were about 0.8 per cent higher than those obtained without shields. For all the calorimeters, with the exception of the Boys, the heating values obtained with shields were higher than without them. The shields were not tried with the luminous flame burner furnished with the Boys calorimeter, but with a glass tube Bunsen burner which was substituted.

The experiments made in May, 1913, which were performed with extreme care under the most favorable conditions, showed that the effect of shields in diminishing heat losses is somewhat less than 0.5 per cent while all the earlier experiments indicate that the effect was 0.5 per cent or more of the total heating value. The results as a whole, however, show the advisability of using shields where high accuracy is sought.

(d) **Conduction Down Stem of Burner.**—The heat lost by conduction down the stem of the Bunsen burner is negligibly small, as may be seen from the following considerations: The area of that part of one of the burners furnished with the Sargent calorimeter, which was outside the calorimeter was estimated as about 40 cm^2. Using the figure already quoted (p. 54) for the heat loss from a nickeled surface per square centimeter per minute per 1° C excess of temperature above surroundings, namely 0.006 calorie, a simple computation shows that the average temperature of the exposed portion of the burner would have to be over 200° F before the loss would amount to 0.1 per cent for a 600 Btu gas, burned at 7 cubic feet per hour. The actual excess of temperature is very small.

(e) **Heat Carried Off By Products of Combustion.**—The products of combustion carry off from the calorimeter sensible heat, proportional to their mass and excess of temperature above that of the entering air and gas, and latent heat, equivalent to the latent heat of vaporization of the excess of water vapor carried out by the products over the water vapor carried in by the air and the gas.

If the calorimeter is operated at the normal rate of gas consumption (see p. 69), so that for illuminating gas (600 Btu) the ratio of volumes of gas to air is about 1 to 7, the amount of sensible heat carried off in the combustion products per 1° F excess of temperature during the combustion of 1 cubic foot of gas is about 0.1 Btu. As it has been shown that the temperature of the products can, in a properly designed calorimeter, be reduced very nearly to that of the inlet water by suitable location of the burner, it follows that the sensible heat carried away by the products may be made negligibly small.

The gas and air entering the calorimeter carry in an amount of water vapor determined by their volumes and their degrees of

saturation, and the products carry out an amount of water vapor determined by their volume and degree of saturation. The observed heating value will, therefore, differ from the total heating value on account of the latent heat carried off in the products, by an amount depending upon the degree of saturation of the entering air and gas and of the escaping products and upon their volumes.

The net heating value determined with the calorimeter will not, however, be affected in this way, as may be seen from the following considerations. The net heating value may be calculated from the total heating value by subtracting from the latter the latent heat of vaporization of the water formed during combustion. If any of the water formed during combustion is condensed in the calorimeter, the water so condensed may be measured and its latent heat of vaporization subtracted from the observed heating value, while the heat of vaporization of the remaining water formed by combustion, and which is carried off in the escaping products, does not appear in the observed heating value. If, for example, a large volume of dry air is drawn into the calorimeter a considerable amount of water vapor, formed in combustion, will be carried out by the resulting large volume of combustion products, and the observed heating value will be correspondingly low. However, a correspondingly smaller amount of water vapor will be condensed and collected, and the quantity to be subtracted from the observed heating value, to obtain the net heating value, will also be correspondingly diminished, so that the net heating value so found will be the same as if a smaller volume of air, or air of higher degree of saturation, had been drawn into the calorimeter.

Accurate determinations of the net heating value of a gas can therefore be made without a knowledge of the atmospheric humidity or of the volume of the entering air and of the escaping products. Experimental data corrobating this statement will be found under the section relating to atmospheric humidity, see p. 72.

Saturation of Entering Air.—The humidity of the air of the calorimetric laboratory was measured with an Assmann aspiration psychrometer,[10] Fig. 12.

Saturation of Gas.—It has been shown in the section on measurement of gas volumes that gas which has been passed through a

[10] Zs. für Instrumentenkunde, **12**, p. 1; 1892.

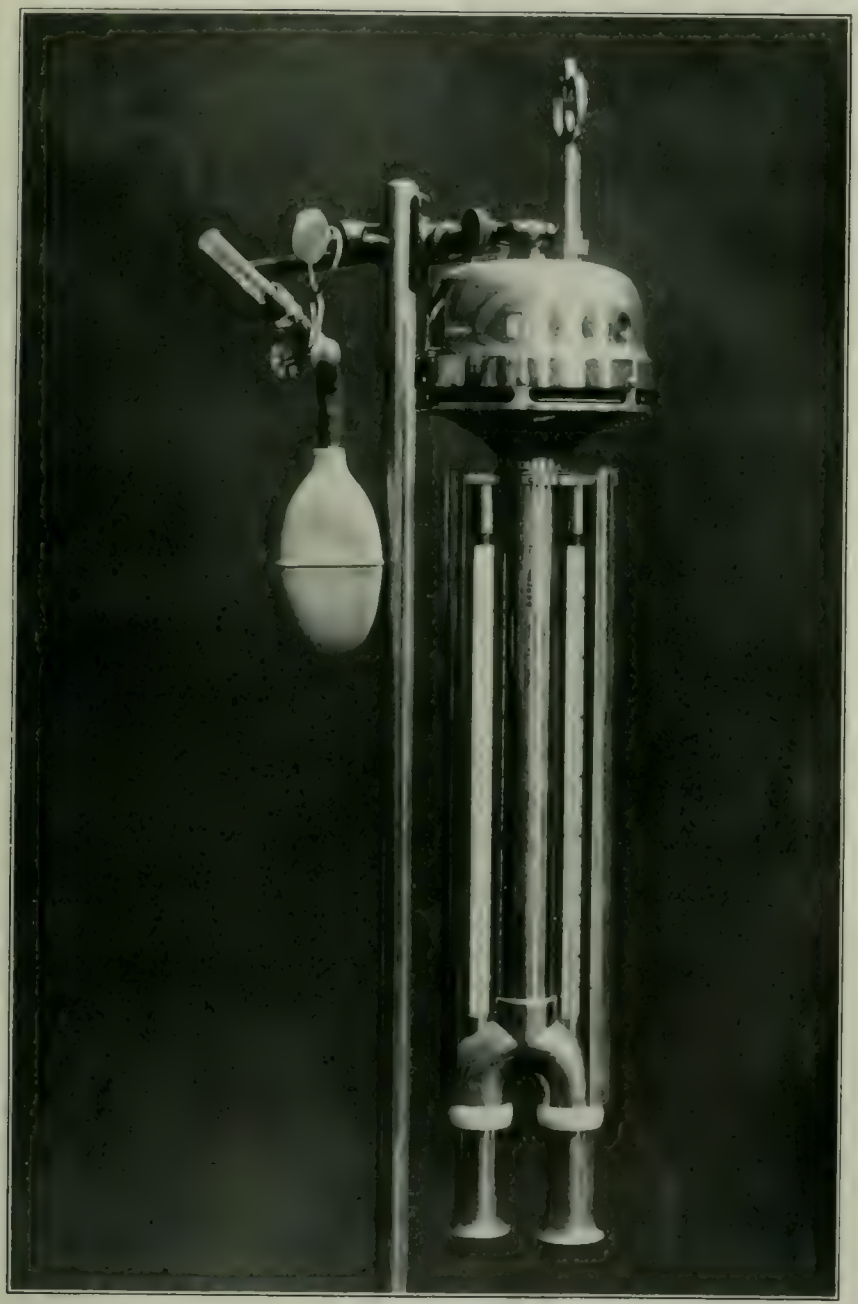


Fig. 12.—*Assmann aspiration psychrometer*

wet meter emerges saturated with water vapor at the temperature of the meter. Wet meters were used in all the experiments, so that the degree of saturation of the gas was always accurately known.

Saturation of Products.—Immenkötter has shown that the temperature at which the combustion products from the Junkers calorimeter are saturated is very approximately that of the inlet water. In the present experiments the saturation temperature of the products was measured by means of a dew-point hygrometer, consisting of a small externally silvered test tube containing mercury and a thermometer with its bulb immersed therein. Cooled mercury was poured into the test tube, the thermometer inserted, and the test tube held in the path of the escaping products. The dew point could be thus determined to an accuracy of about 1° F. In the earlier experiments with the Junkers calorimeter the products were reheated at the base of the calorimeter several °F before escaping from the outlet, owing to the burner not being set high enough. The saturation temperature of the products under these conditions was found to be from a few tenths to 1° F above that of the inlet water. The amount by which the observed saturation temperatures differed from inlet-water temperatures was almost within the limits of error of these experiments, although the small observed differences may have been real ones due to the reheated products taking up water vapor. In the later experiments, in which reheating of the products was avoided by modifying the burner support and raising the burner about 1.5 inches, the saturation temperature of the products must have been even more nearly equal to the temperature of the inlet water.

Volume of Entering Air and of Products.—If either the volume of the entering air or of the escaping products be known, and an analysis of the gas be available, the other may be determined. For the accuracy necessary for correcting observed heating values to total heating values, the following relations between these volumes may be used, assuming that the water formed in combustion is condensed to the liquid state:

If hydrogen is burned, volume of products = volume of air − 0.5 volume of hydrogen.

If illuminating gas is burned (550–650 Btu) volume of products = volume of air − 0.4 volume of gas.[11]

If natural gas (principally methane, CH_4) is burned, volume of products = volume of air − volume of gas.

In this investigation three methods of measuring the volume of air or of products were used (*a*) supplying air through a meter to the closed bottom of the combustion chamber, (*b*) determination of the volume of CO_2 formed by combustion of unit volume of the gas and analysis of CO_2 content of combustion products, and (*c*) measurement of velocity of combustion products through outlet tube of known area.

The arrangement for supplying measured volumes of air to the calorimeter is shown diagramatically in Fig. 15, and described on page 72.

In the products analysis method, the volume of CO_2 resulting from the combustion of a known volume of the gas was first measured and the percentage of CO_2 contained in the combustion products was next determined. From these data the volume of products was directly computed.

In the velocity of products method, it was necessary to use some instrument for measuring velocities, the use of which would not interpose sufficient resistance to appreciably change the velocity to be measured. For this purpose use was made of the fact that the *lag of a thermometer* in a gas varies with the velocity of the gas past its bulb. The details of the method need only be briefly outlined here, as the subject of thermometric lag has been fully treated in a paper by Dr. D. R. Harper 3d.[12] The method was applied as follows:

An extension tube about 8 inches long was fitted to the outlet products tube of the Junkers' calorimeter to insure greater uniformity of velocity of the products over the section of the tube, after their passage through the holes in the damper (when the damper was closed). The uniformity of velocity distribution was further promoted by mounting two small circular gauze diaphragms, about 0.5 inch in front of the damper opening, in such a way as not to appreciably obstruct the flow of the products. A

[11] Examination of a number of published analyses of illuminating gases of different character has shown that this relation may vary between the limits vol. products = vol. air − 0.2 vol. gas and vol. products = vol. air − 0.6 vol. gas. The former relation represents the smallest contraction of volume found for carburetted water gas, and the latter relation the largest contraction in volume found for coal gas.

[12] Bulletin, Bureau of Standards, 8, p. 659; 1912 (Reprint No. 185).

support was so arranged that a thermometer laid in it was in the axis of the extension outlet tube, the bulb being about 2 inches within the tube.

The calibration of this arrangement was made by passing air through the calorimeter at known rates, as measured by a gas meter previously calibrated at these rates, and determining the corresponding *lags* of the thermometer. The procedure was as follows: After the flow of air was started, the thermometer was placed in the support and left there for some minutes until its reading gave the temperature of the issuing air (water at room temperature flowing through the calorimeter kept this tempera-

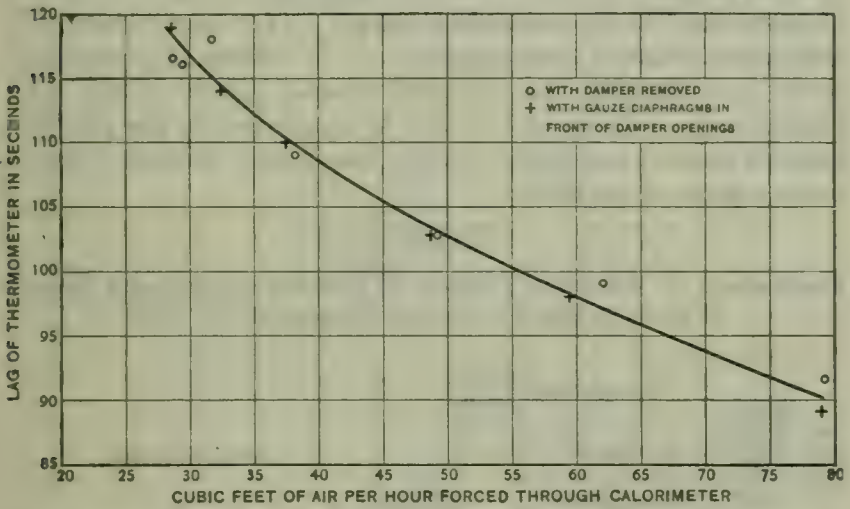


Fig. 13.—*Lag of thermometer No. 77874 vs. volume of air forced through Junkers calorimeter No. 1209*

ture constant); the thermometer was then warmed about 15° C by dipping into a beaker of warmed mercury and was then quickly transferred to the support above mentioned and, with the aid of a stop watch, the times were observed at which its readings were 10°.00 C and 3°.68 C, respectively, above the temperature of the issuing air. The time, in seconds, elapsing between these two readings of the thermometer is defined as the lag of the thermometer. A curve showing the relation between volume of air passing through the calorimeter and the lag of thermometer No. 77874, placed in the extension outlet tube, is shown in Fig. 13.

The operation of finding the volume of products escaping from the calorimeter under the conditions of use (i. e., gas burning and air drawn in by convective circulation) consisted in measuring the lag of the thermometer, in the manner just described, and in reading from the curve the corresponding volume of escaping products.

A large amount of data relating to the measurement of the volume of products escaping from the calorimeter, when air was drawn in by the action of the flame, has been obtained for a number of calorimeters under varied conditions of use, both by the products analysis method and the velocity of products method. The order of agreement of the methods is about 10 per cent, which is a sufficiently accurate determination of the volume of products to serve for correcting the observed heating value to the total heating value. Table 16 is a sample comparison of the products analysis method and of the velocity of products method of measuring volume of products.

TABLE 16

Measurement of Volume of Products by Products Analysis and Velocity of Products Methods, Junkers Calorimeter No. 1209

Experiment No.	Rate of gas consumption, cubic feet per hour	Values of Ratio $\frac{\text{Vol. products}}{\text{Vol. gas}}$				Conditions of operation
		By velocity of products			By products analysis	
		Thermometer No. 80659	Thermometer No. 77874	Mean		
1	7.1	5.9	5.7	5.8	5.7	Damper closed.
2	3.6	9.7	9.8	9.8	9.3	Do.
3	3.6	17.1	15.7	16.4	15.4	Damper open.
4	7.1	10.2	9.4	9.8	8.6	Do.

Under whatever conditions the calorimeter may be used, as to rate of gas consumption, damper opening, etc., provided that combustion is complete, it is possible, if the volume of the products, their humidity and that of the entering air be known, to apply the corrections necessary to reduce observed heating values to total heating values. Such data were obtained for a number of calorimeters. The results of a typical series for the Hinman-Junkers

calorimeter No. 91 are shown by the curves of Fig. 14. As appears from the curves, the rate of gas consumption was varied from 3 cubic feet to 12 cubic feet per hour, the calorimeter being operated with open damper. The volume of air varied from about 60 cubic feet per hour, for a gas consumption of 3 cubic feet per hour, to 85 cubic feet per hour for a gas consumption of 12 cubic feet per hour—i. e., increasing the gas supply four times—all other conditions remaining unchanged, increased the air supply by only about 40

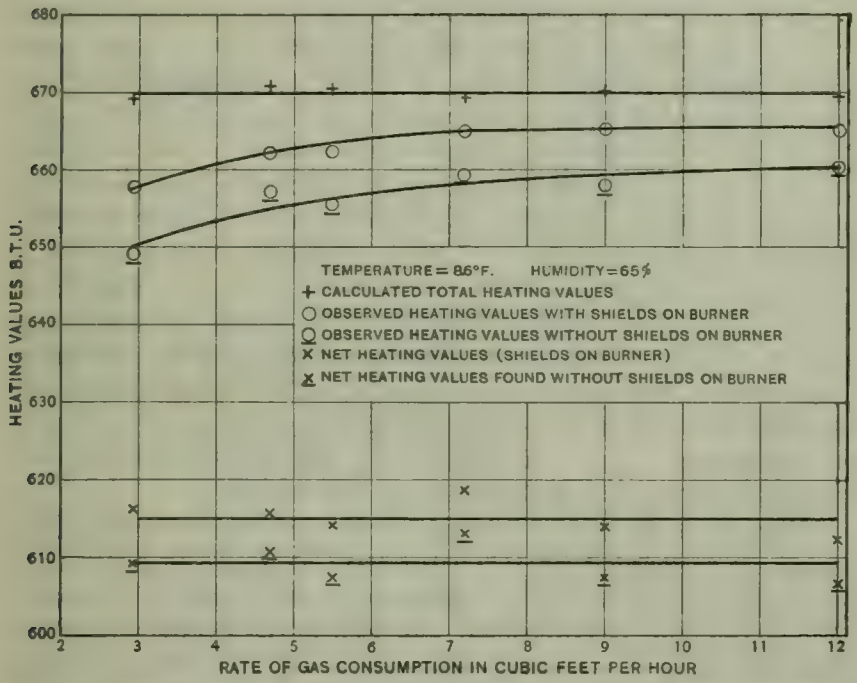


Fig. 14.—*Heating values found with Hinman-Junkers calorimeter No. 91, operated with open damper at various rates of gas consumption*

per cent, and most of this relatively small increase in air supply occurred at low rates (between 3 and 7 cubic feet of gas per hour). It appears from the above that at the low rate of gas consumption, a large excess of air was drawn into the calorimeter (ratio of volumes air to gas = 20), while at the highest rate only a small excess of air was drawn in (ratio of volumes air to gas = 7).

The method of correcting observed to total heating values is discussed on page 74. Fig. 14 shows that the various observed

heating values all lead to the same total heating value. The net heating values found are also in agreement to within the limits of experimental errors. Fig. 14 also shows the decrease in heat loss due to the use of radiation shields. That the increase in the heating values found with shields is not due to diminished air supply is shown by the fact that the net heating values are increased by the use of shields to practically the same extent as are the observed heating values.

Curves of the type shown in Fig. 14, giving a relation between observed heating values and rates of gas consumption, have been called *capacity-efficiency curves*. It is well to emphasize the fact that the form of these curves depends upon the conditions of operation of the calorimeter—e. g., whether the damper is open or closed, and if closed, the number of openings in the damper and their total area, and upon the humidity and temperature of the air at the time the experiments are made. If the experiments were made on a day of very high humidity, the curve would be a nearly horizontal straight line—i. e., observed heating values would be nearly the same at all rates of gas consumption up to the point of incomplete combustion. The lower values observed at low rates of gas consumption are due to the correspondingly high values of the ratios of volumes air to gas (and products to gas) and to the relatively greater importance of surface losses at the low rates.

Attention is directed to this matter for the reason that the committee on calorimetry of the American Gas Institute have published a number of capacity-efficiency curves for different calorimeters and have recommended operating the calorimeters at or near their point of maximum efficiency as shown by these curves. Thus, in the published curve for the Junkers calorimeter, this corresponds to a rate of about 7.5 cubic feet of gas per hour. The point which should be emphasized is that the curve referred to was obtained by operating the calorimeter with the damper closed, said damper having two openings, each 15 mm diameter. The capacity-efficiency curve of this calorimeter, operated with open damper, was found to be quite different from that obtained with the damper closed.

Fig. 14, as well as other data in this report, show that even at the maximum efficiency rate of gas consumption, the observed heating value will, in general, differ from the total heating value.

"Normal Rate" of Gas Consumption—Ratio of Air to Gas at the Normal Rate.—As will be shown in the following section, the correction from observed to total heating value is very simply made if the volumes and degree of saturation of air and of products be known, the magnitude of the correction depending upon the excess (or deficiency) of the water vapor carried out over that carried into the calorimeter. For the operation of calorimeters a suitable rate for the combustion of the gas, which will be called the *normal rate*, as well as the approximate values of the ratios air to gas and products to gas, may be found by the application of the following rule: Determine the rate of gas consumption at which combustion begins to be incomplete, and operate the calorimeter at 70 per cent of that rate. This will be the *normal rate* for the calorimeter and gas in question, for the conditions (damper opening, etc.) under which the calorimeter was operated.

The choice of the rate at which the calorimeter is to be operated is necessarily an arbitrary one. The rate of 70 per cent of that at which combustion begins to be incomplete was chosen for the following reasons: (*a*) At this rate the capacity-efficiency curves are approximately horizontal, so that the rate need not be very exactly fixed; (*b*) the rate is not so great as to make it probable that the combustion will be incomplete.

The rates for the different calorimeters, when determined by this rule, correspond approximately to those recommended by the committee on calorimetry of the American Gas Institute.

It has been found, both from products analyses and from measurements of the velocity of the products, that at the normal rate the volume of air drawn into the calorimeter is about 40 per cent in excess of that theoretically required for combustion as calculated from the chemical composition of the gas. For example, with an illuminating gas of about 650 Btu, the ratio of volumes air to gas at the normal rate of gas consumption is about 7 to 1; for natural gas of about 1000 Btu this ratio is about 12 to 1.

A convenient procedure for determining the rate at which combustion is no longer complete is as follows: With the calorimeter in operation, the rate of gas consumption is increased step by step, e. g., by successively increasing the load on the pressure regulator by adding weights. As long as combustion is complete,

the effect of increasing the gas rate is to cause an increment in the reading of the outlet-water thermometer. However, when the gas rate attains a value such that combustion is no longer complete, there will be a decrement in the reading of the outlet-water thermometer, accompanying an increase in the gas rate. The gas rate at which combustion begins to be incomplete (for a given damper setting, etc.) can thus be determined to within a few per cent. An almost equally good test is furnished by the odor of the combustion products, as the odor due to incomplete combustion is readily perceived for most gases.

To determine whether the normal rate was dependent upon the temperature rise of the water flowing through the calorimeter, the following experiments were tried: The Junkers calorimeter No. 1209 with damper closed, said damper having two openings, each 13 mm diameter, was operated so that the temperature rise of the water in successive tests was 14°, 25°, 36°, and 49° F, respectively. In each test the rate of gas consumption at which combustion began to be incomplete was determined in the manner already explained and was found to be approximately 8 cubic feet per hour for all of these temperature rises of the water. Hence the normal rate was independent of the temperature rise of the water in the calorimeter and was equal to $0.70 \times 8 = 5.6$ cubic feet per hour for the Junkers calorimeter No. 1209 operated with the special damper described above and with the illuminating gas (about 650 Btu) used in these tests.

If the facilities for making a gas analysis are available, the ratio of volumes products to gas may be determined for the normal rate of gas consumption by the method of products analysis previously referred to; but if such an analysis is not available, the method given above for determining the value of the ratio of volumes, air to gas, is sufficiently accurate for the purpose of reducing observed heating values to total heating values. That this is true has been shown by the data obtained in the intercomparison of a number of different gas calorimeters of the flow type. These intercomparisons showed that when the various calorimeters were each operated at their normal rate, as determined by the above rule, the total heating values obtained were identical, within the limits of experimental error; and, further, that the amount of water vapor

condensed and collected, per cubic foot of gas burned, was the same.

A further check on the applicability of the rule was obtained by means of the following experiment: Three dampers, each having two openings of 13, 15, and 17 mm diameter, respectively, were successively used with the Junkers calorimeter No. 1209. The results obtained in this experiment are given in Table 17.

TABLE 17

Junkers Calorimeter Operated at Normal Rates of Gas Consumption with Different Dampers

Damper used	Normal rate [13]	Water condensed per cubic foot of gas burned	Total heating value, Btu	Net heating value, Btu
	cu. ft. hr.	cc		
13 mm openings	5.5	21.0	656	606
15 mm openings	7	21.0	656	606
17 mm openings	8	21.2	658.5	607.5
Damper removed	10	20.8	656.5	607
			657	607

[13] Determined by the rule that normal rate = 70 per cent of rate at which combustion begins to be incomplete.

Further data in support of applicability of the method given for determining the value of the ratio of volumes, air to gas, was obtained from the following experiments. Illuminating gas of 650 Btu was burned in the Junkers calorimeter at the normal rate of 7 cubic feet per hour. The volume of products measured by the thermometer lag method was found to be 45 cubic feet per hour. The corresponding volume of air being 48 cubic feet per hour (i. e., $45+0.4\times7$) gave a ratio of volumes air to gas of practically 7 to 1. The gas required about 5 cubic feet of air per cubic foot of gas to furnish the oxygen necessary for combustion. The amount of air drawn in was therefore in this case very nearly 40 per cent in excess of that required. When natural gas of 1000 Btu was burned in the same calorimeter at a normal rate of 4.1 cubic feet per hour the ratio of volumes products to gas was found by products analysis to be 10.5 to 1, while computation (assuming 40 per cent excess of air at the normal rate) gave a ratio of 11 to 1.

The "maximum-efficiency" rates determined by the committee on calorimetry of the American Gas Institute with illuminating gas (about 600 Btu) for a number of calorimeters are practically identical with the normal rates for the same calorimeters, operated under similar conditions and with the same kind of gas. It is important, however, to call attention to the fact that neither the "maximum-efficiency" rate nor the normal rate are constants of the calorimeter, but vary with the conditions of operation (principally damper opening) and with the character of the gas burned (natural, illuminating, producer, etc.). The rule for determining the normal rate takes all these factors into account and gives sufficient information as to the values of the ratios air to gas and products to gas, so that the necessary corrections to obtain total heating values can be determined and applied. The normal rate can also be more simply and precisely determined than can the "maximum efficiency" rate.

(f) **Effect of Atmospheric Humidity.**[14]—In determining net heating values with a flow calorimeter, no account need be taken of atmospheric humidity. However, the observed heating value found will be affected by the humidity and volume of the entering air. This effect may readily be observed on a day of low humidity by opening the damper, when the observed heating value will be found to be lower than with the damper closed. The decrease in the observed heating value is due to the fact, that with the damper open, the air supply is increased, and more of the water formed by combustion is carried out as vapor in the escaping products.

The following experiments were devised to show quantitatively the effect of the humidity and volume of the entering air on the observed and on the net heating values. A diagrammatic sketch of the arrangement of the apparatus used is shown in fig. 15. A glass ring 2 inches high and 2.5 inches in diameter was fastened to the base of the Junkers Calorimeter with soft wax. This ring was closed at the bottom by a brass plate, through which extended the burner and a three-fourths inch tube to admit the air supply. The air was distributed within this cell by means of a cylinder

[14] The effect of atmospheric humidity on the results of heating value determinations with flow calorimeters has been considered for some special cases by Coste (J. Soc. Chem. Ind. 28, p. 1231; 1909) and by Parr (J. Ind. and Eng. Chem., 2, p. 337; 1910) and somewhat more generally by Holgate (J. Gas Lighting, London, 109, p. 355; 1910).

with gauze sides and closed at the top, and which fitted over the air inlet. A small inclined mirror on the brass plate was used for observing the flame. With the air distributor in position, the character of the flame was normal. Air taken from the laboratory pressure system was passed through a pressure regulator A, a meter B, a saturator C, consisting of a closed metal box with inlet and outlet tubes and containing water kept at a temperature of about 100° F by a burner, through a brass tube condenser D, containing brass turnings in its central tube, and supplied with water at room temperature from the thermostat, and thence into the

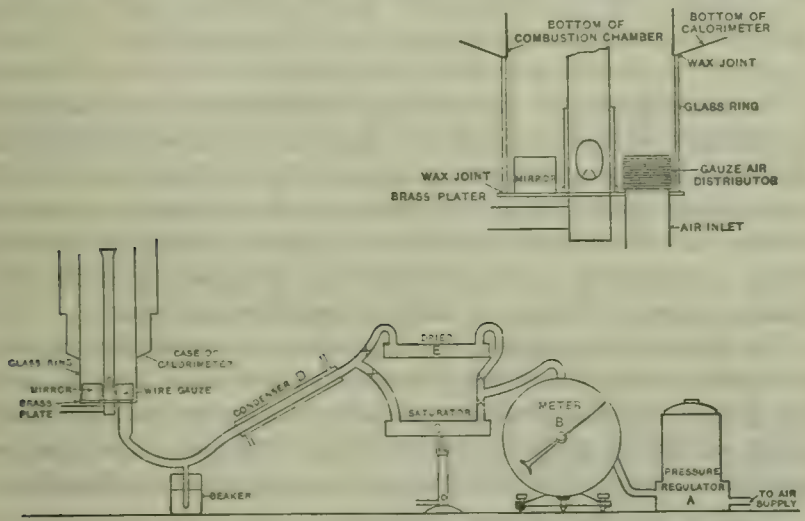


Fig 15.—*Arrangement of apparatus for supplying measured volumes of saturated or of dried air to a calorimeter*

calorimeter through the inlet tube described above. By means of this system air, saturated at inlet water temperatures, was supplied to the calorimeter. The saturator could be replaced by a drier, E, so as to supply to the calorimeter air of very low humidity and at inlet water temperature.

The results of a typical series of experiments are summarized in Table 18. In this table certain small constant corrections, such as those for heat losses from the surface, etc., which are applied in the reductions given on page 22. have been omitted, as they affect all the results equally.

TABLE 18

Effect of Volume and Humidity of Air on Heating Values, Junkers Calorimeter No. 1209 (Oct. 25, 1911)

Experiment No.	Gas burned, cubic feet per hour	Air supplied, cubic feet per hour	Humidity of air at 69° F.	Water, condensed, per cubic foot of gas burned	Observed heating value	Net heating value	Total heating value
			Per cent	cc	Btu	Btu	Btu
1	4.6	34.7	100	24.1	663.0	608	661
2	4.6	34.7	15	22.2	658.2	607	664
3	4.6	34.0	15	21.9	657.5	607	663
4	4.6	50.0	15	19.8	651.9	606	661
Mean						607	662

The table shows (*a*) that the net heating values are unaffected by changes in the amount and humidity of the entering air; (*b*) that when proper allowance is made for the latent heat of the water vapor carried off in the products of combustion, observed heating values obtained under widely varying conditions and differing considerably among themselves, all give the same total heating value to within the limits of experimental error.

The following example is given to show the method of calculation used in computing the correction which must be applied to the observed heating values to allow for the latent heat of vaporization of that part of the water which is formed in combustion and which is carried off as vapor in the products of combustion:

Example: Junkers calorimeter No. 1209.
Illuminating gas burned at normal rate=7 cubic feet per hour.
Temperature of room, meter, inlet water, and products=60° F.
Barometric pressure=30 inches.
Humidity of air=40 per cent.
Ratio of volumes air to gas=7.
Ratio of volumes products to gas=6.6.
Average temperature of outlet water=78° F.
Water vapor condensed and collected per cubic foot of gas burned=21.0 cubic centimeters.
Observed heating value=648.3 Btu.

1 cubic foot of saturated water vapor at 60° F weighs	0.372 grams.
Water vapor carried in by air per cubic foot of gas burned= $0.372 \times 0.40 \times 7$	=1.04 grams.
Water vapor carried in by 1 cubic foot of gas	= .37 grams.
Total water vapor carried in per cubic foot of gas burned	=1.41 grams.

Example—Continued

Water vapor carried out in products per cubic foot of gas burned = 0.372 × 6.6 = 2.46 grams.

Excess water vapor carried out per cubic foot of gas burned = 1.05 grams.

Heat of vaporization of excess = 1.05 × 2.3 = 2.4 Btu.

Hence the heating value, corrected for the excess of water vapor carried out, is 648.3 + 2.3 = 651 Btu.

In the actual use of the calorimeter this computation need not be made for each observation, but the correction may be taken from Table 19 by entering the table with the arguments, temperature = 60° F, humidity = 40 per cent. Although in actual operation the equality of room temperature, meter temperature, inlet water temperature, and products temperature will not be exactly realized, the departure from this condition may be easily kept within limits such that no significant error will arise from the use of the table. This will be evident on inspection of the table, where it appears that the correction, for a given atmospheric humidity, changes rather slowly as the temperature changes.

In the computation of Table 19 the simple process used in the above example was modified to take account of the variation in the volumes of air, gas, and products, due to their water vapor content. Since it is the volume of products which is limited by the damper openings, the most reasonable assumption seemed to be that for the normal rate of gas consumption the ratio of volumes products to gas (rather than the ratio of volumes air to gas) would remain constant. The constant value taken for this ratio was 6.6, and the corresponding volume of air was calculated on the assumption that the volume of saturated air is given by the relation, volume of products = volume of air − 0.4 volume of gas. The simpler assumption made in the example given above, that both the ratios of volumes, air to gas and products to gas, are constant, is inconsistent, but would lead to no errors that are significant so far as the accuracy attainable with flow calorimeters is concerned. The tabular values are so calculated as to be directly applicable to observed heating values (where that term has the meaning assigned on p. 14) provided the measurements are actually made at a barometric pressure of 30 inches. If the measurements are made at a place where the barometric height,

H, differs considerably from 30 inches, the tabular corrections must be multiplied by the factor $\frac{30}{H}$ before being applied to the observed heating values. The tabular corrections are, however, directly applicable to heating values calculated to a temperature of 60° F and prevailing local barometric pressure.

The assumption that the relation between the volumes of air, gas, and products will be that used in computing this table, and that when gas is burned in the calorimeter at the normal rate the ratio of volumes, products to gas, will be equal to 6.6, are of course only approximately correct. The error in the first assumption would cause no appreciable change in the table. So long as the first assumption is valid any error in the second would not affect the correctness of the tabular values for 100 per cent humidity, but would affect the values for the lower humidities. For example, if the ratio of volumes, products to gas, were 7.6 instead of 6.6, the tabular correction for 40° F and 10 per cent humidity would be too small by less than 0.5 Btu, while the tabular correction for 90° F and 10 per cent humidity would be too small by about 2 Btu.

It is not probable, however, that under most conditions of testing the ratio of volumes products to gas would, when illuminating gas was burned at the normal rate, differ by much more from 6.6, than is assumed in the above example.

When the calorimeter was operated at normal rate of gas consumption and natural gas of high methane content (950–1000 Btu) was burned, it was found that the ratio of volumes products to gas was about 11 to 1 (the corresponding ratio of saturated air to gas being about 12 to 1). Table 20 is applicable to calorimetric determinations on natural gas under the same conditions as are stated above for Table 19 for illuminating gas.

In view of the ease with which the correction for effect of atmospheric humidity may be applied to observed heating values found with flow calorimeters operated at the normal rate, it seems inadvisable to complicate the apparatus by the addition of devices having for their object the saturation of the air entering the calorimeter, especially so since, even with a saturator, a correction to the observed heating value would still be necessary unless the air were delivered to the calorimeter at about 80 per cent saturation.

TABLE 19

Corrections, in Btu, to be Applied to Observed Heating Values in Calculating Total Heating Values of Illuminating Gas (about 600 Btu)

[The tabular corrections are applicable when inlet water, air, gas, and products are all at approximately the same temperature, and when the calorimeter is operated at *normal rate* of gas consumption (see p. 69).]

Temperature of room, etc.	Relative humidity of air									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
°F										
40	+ 2	+ 2	+ 1	+1	+1	+1	0	0	0	−1
45	+ 2	+ 2	+ 2	+1	+1	+1	0	0	0	−1
50	+ 3	+ 3	+ 2	+2	+1	+1	0	0	0	−1
55	+ 3	+ 3	+ 3	+2	+1	+1	+1	0	0	−1
60	+ 4	+ 4	+ 3	+2	+2	+1	+1	0	0	−1
65	+ 5	+ 4	+ 4	+3	+2	+2	+1	0	−1	−1
70	+ 6	+ 5	+ 4	+3	+3	+2	+1	0	−1	−2
75	+ 7	+ 6	+ 5	+4	+3	+2	+1	0	−1	−2
80	+ 8	+ 7	+ 6	+5	+4	+3	+1	0	−1	−2
85	+10	+ 9	+ 7	+6	+4	+3	+2	0	−1	−3
90	+12	+10	+ 9	+7	+5	+4	+2	0	−2	−3
95	+14	+12	+10	+8	+6	+4	+2	0	−2	−4

TABLE 20

Corrections, in Btu, to be Applied to Observed Heating Values in Calculating Total Heating Values of Natural Gas (about 1000 Btu)

[The tabular corrections are applicable when inlet water, air, gas, and products are all at approximately the same temperature, and when the calorimeter is operated at *normal rate* of gas consumption (see p. 69).]

Temperature of room, etc.	Relative humidity of air									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
°F										
40	+ 4	+ 3	+ 3	+ 2	+ 2	+1	+1	0	0	−1
45	+ 4	+ 4	+ 3	+ 3	+ 2	+1	+1	0	0	−1
50	+ 5	+ 5	+ 4	+ 3	+ 3	+2	+1	0	0	−1
55	+ 6	+ 6	+ 5	+ 4	+ 3	+2	+1	0	−1	−1
60	+ 8	+ 7	+ 6	+ 4	+ 3	+2	+1	0	−1	−2
65	+ 9	+ 8	+ 7	+ 5	+ 4	+3	+2	0	−1	−2
70	+11	+ 9	+ 8	+ 6	+ 5	+3	+2	+1	−1	−2
75	+13	+11	+10	+ 8	+ 6	+4	+3	+1	−1	−3
80	+15	+13	+11	+ 9	+ 7	+5	+3	+1	−1	−3
85	+18	+16	+13	+11	+ 9	+6	+4	+1	−2	−4
90	+21	+19	+16	+13	+10	+7	+4	+1	−2	−5
95	+25	+22	+19	+15	+12	+8	+5	+1	−2	−6

4. TEMPERATURE OF INLET WATER

It has already been mentioned that it is preferable to operate the calorimeter with the inlet water at the temperature of the room and to make corrections for the heat losses that occur under this condition of operation. If the temperature of the inlet water differs from that of the room, the conditions of heat interchange and the amount of heat carried off in the products of combustion will differ from what they would be if the inlet water were at room temperature. It is evident that if, with the calorimeter operated with inlet water at room temperature, the observed heating value is lower than the total heating value, it should be possible, by operating with the inlet water at some lower temperature, to obtain an observed heating value that should be identical with the total heating value. This method has been recommended by Parr [15] and has been extensively used elsewhere.[16] Parr, after giving an excellent analysis of the problem, unfortunately reaches the conclusion that, in using the Junkers calorimeter, the heat losses can be compensated under all conditions by operating the calorimeter with the inlet water at a temperature such that the exhaust gases leave the calorimeter at a temperature of 10° to 12° F below that of the room. In view of the importance given the subject, an extensive series of experiments to determine the effect of varying the inlet water temperature was made with two calorimeters, Junkers No. 1209 and Junkers No. 871, the latter kindly placed at the disposal of the Bureau for this purpose by Prof. O. L. Kowalke, of the University of Wisconsin.

Since the heat of combustion of a cubic foot of a given gas is a definite quantity, this value should be calculable from data obtained with the inlet water at various temperatures, provided corrections were made to take account of the following factors:

(*a*) Variation of the specific heat of water.
(*b*) Heat interchange with surroundings.
(*c*) Sensible heat carried off in products.
(*d*) Sensible heat carried off by condensed water.
(*e*) Latent heat of water vapor in products.

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[15] J. Industrial and Engineering Chemistry, 2, p. 337; 1910.
[16] Report of Calorimetry Committee American Gas Institute, 1912.

In Fig. 16 are plotted, for a given sample of gas, the heating values obtained in a series of determinations with the Junkers calorimeter No. 1209, operated with the inlet water at various temperatures. The calorimeter was operated at the normal rate, so that the volume of products was approximately determined by this condition. It will be seen that the observed values, when corrected as indicated above, all lead to practically the same total heating value. Similar results were obtained with Junkers calorimeter No. 871. The point at which the observed heating

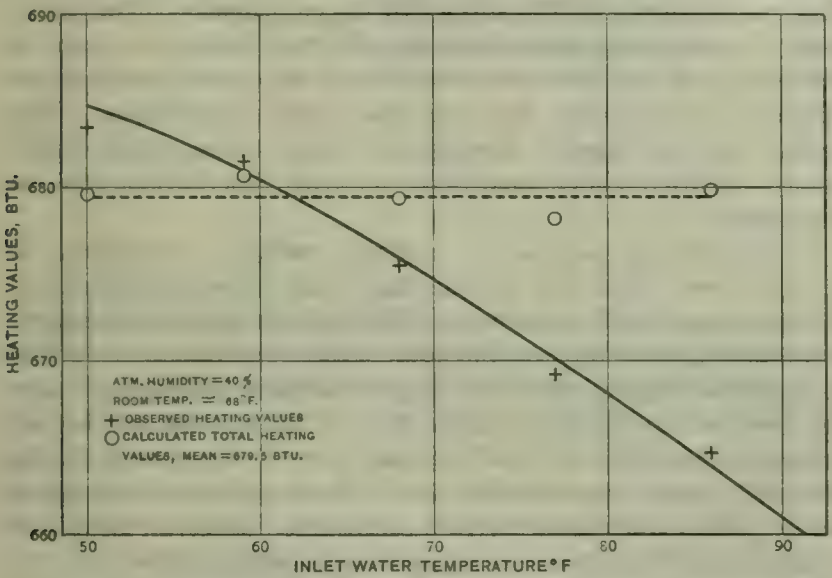


Fig. 16.—*Heating values found with Junkers calorimeter No. 1209, operated with inlet water at various temperatures*

value, under the conditions of humidity, etc., prevailing during this experiment, is the same as the total heating value is seen to be where the inlet water is about 6° F below the temperature of the room. As will be seen from the section on Effect of Atmospheric Humidity and from Table 19, conditions are possible under which it would be necessary to operate the calorimeter with the inlet water somewhat above room temperature, in order that the observed heating value should be identical with the total heating value. In other words, a constant difference of temperature between

exhaust gases and room temperature, as suggested by Parr, can not be used, but a table would have to be calculated giving the required difference for various degrees of atmospheric humidity and for different room temperatures.

An experiment made with a Simmance Abady (American type) calorimeter to determine the effect of operating with inlet water below the dew point of the surrounding atmosphere, indicated that there was no significant change at this point in the rate at which the calorimeter gained heat from the surroundings, although dew was deposited on the surface of the calorimeter. The above type of calorimeter was chosen for the test because its rate of interchange of heat with the surroundings, for a given temperature difference, was larger than for the other calorimeters. This matter was not further investigated, since calorimeters should not be operated under conditions in which dew is deposited on the surface.

It is evidently possible, by applying suitable corrections, to obtain correct total and net heating values from data obtained by operating a flow calorimeter with the inlet water at temperatures differing from that of the room. The correction to be applied to the total heating values on account of such difference of temperature will be different from that to be applied to the net heating values, due to the fact that part of the change in the observed heating value is due to a difference in the amount of water vapor condensed in the calorimeter, a factor which is eliminated in the determination of the net heating value.

The correction per 1° F difference between inlet water temperature and room temperature to be applied in the calculation of total and of net heating values will depend upon the room temperature. The corrections would be the same for all the calorimeters if it were not for the difference in the losses of heat from the surfaces. Since the effect of heat interchange with the surroundings is rather a small part of the total corrections, a table of corrections applicable without sensible error for all the flow calorimeters of the ordinary type may be computed by taking into account the five factors enumerated at the beginning of this section.

In Table 21 are given for various room temperatures the amounts per 1° F difference between room temperature and inlet-water temperature by which the total and the net heating values, calculated as if the inlet water had been at room temperature, must be corrected on account of such differences of temperature.

TABLE 21

Corrections per 1° F Difference Between Inlet Water Temperature and Room Temperature for Conditions Stated Above

Room temperature	Corrections in Btu for calculating total heating value	Corrections in Btu for calculating net heating value
°F		
50	0.5	0.4
60	.6	.4
70	.7	.4
80	.8	.4
90	.9	.5
100	1.0	.5

The corrections calculated from this table may be applied, without sensible error, to heating values of illuminating gas (about 600 Btu) determined with any of the flow calorimeters listed in this report (except the Doherty calorimeter), the correction being added if the inlet water is warmer than the room and subtracted if the inlet water is colder. The tabular values are average values for all the calorimeters, and are therefore slightly too large for the Junkers, Sargent, and Hinman-Junkers calorimeters and somewhat too small for the Simmance-Abady and Boys calorimeters. However, the error due to use of the tabular corrections will be unimportant for any of the calorimeters mentioned, for moderate differences of temperature (not over 10° F).

5. CONSTANCY OF FLOW OF WATER AND OF GAS; EFFICIENCY OF GAS PRESSURE REGULATORS

The effect on the readings of the outlet-water thermometers, due to variations (caused mainly by entrapped air) in the rate of flow of water through the calorimeter, has been considered on page 44.

Gas Pressure Regulators.—Two types of pressure regulators are in general use, the balance type and the float type, which are illustrated in Fig. 17. The former may be compensated for variable immersion. The latter was found to be satisfactory and was used throughout the present investigation. To obtain some idea of the efficiency of this type of regulator in reducing fluctuations of gas pressure, the following experiments were tried.

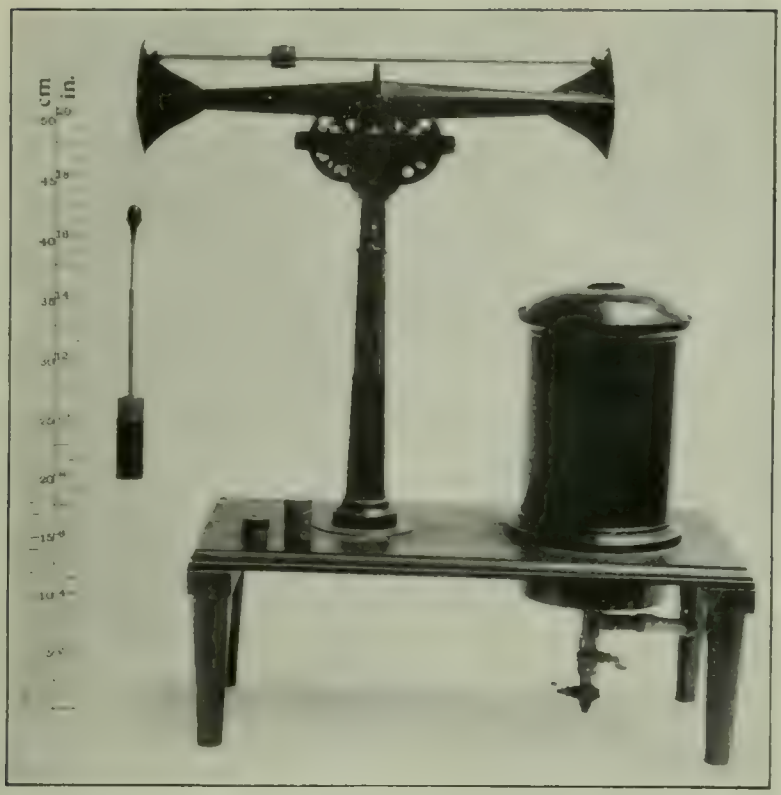
A meter, a regulator, and a burner were connected in series and the inlet pressure at the meter was varied from 1.5 to 6 inches of water. It was found that the amount of gas delivered (making allowance for the difference in pressure at which it was metered), as determined by timing the meter, was about 2 per cent less at the higher inlet pressure. The pressure maintained at the burner tip by the regulator was about 0.7 inch. The efficiency of pressure regulation may depend somewhat upon the amount of this pressure.

When two pressure regulators were used, one ahead of the meter and another between the meter and the burner, changing the inlet pressure on the first regulator from 1.5 to 6 inches of water produced a decrease of 0.5 per cent in the rate of gas delivery.

A series of experiments in which the weights on the regulator were removed and replaced, the float depressed, etc., while the pressure on the system was kept constant, showed that the regulator could not be relied upon to maintain a constant flow of gas over a considerable period of time to better than about 0.5 per cent. However, such variations of gas flow would introduce no serious error into a calorimetric measurement in which simultaneous measurements are made of the water flow and the gas flow.

If only one pressure regulator is used, it will usually be preferable to connect it between the gas supply and the meter rather than between meter and burner, as the inlet pressure at the meter will then be practically constant from day to day, and the small movements of the float, with their resulting variations in volume, will introduce no errors in the assumption that the volume of gas measured is equal to that burned.

If a float regulator of the usual type furnished with flow calorimeters is used, a difference in the position of the float amounting to one-sixteenth inch at the beginning and end of an experiment



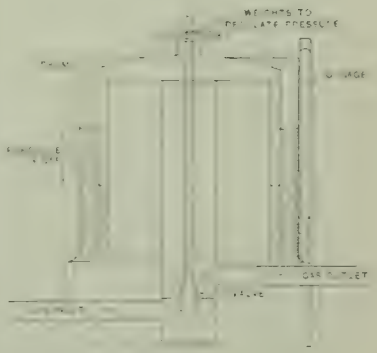


Fig. 17.--*Gas pressure regulators, balance and float types*

in which 0.2 cubic foot of gas is burned will cause an error in the result of about 0.3 per cent. It is therefore safer not to connect such a regulator between the meter and the burner unless the pressure at the meter inlet is kept constant, e. g., by another regulator, an arrangement which for several reasons is the most satisfactory.

The fluctuations in the readings of the outlet-water thermometer of the calorimeter were apparently no greater when the regulator was connected between the meter and the gas supply than when it was connected between the meter and the burner.

The experiments cited, as well as the results obtained in connection with the use of these regulators with calorimeters, show that such regulators will maintain the pressure sufficiently constant, so that no significant error will be introduced due to the effect of fluctuations of gas rate. The regulation is not sufficiently good, however, to warrant calculation of heating values from observations of the rate of water flow and of gas flow, instead of the usual procedure of determining the amount of water collected during the combustion of a measured volume of gas.

6. TIME REQUIRED FOR THE ATTAINMENT OF THERMAL EQUILIBRIUM IN FLOW CALORIMETERS

An essential condition for the correct measurement of heating values with flow calorimeters is that thermal equilibrium shall have been established before the measurements are begun, i. e., that none of the heat supplied during the period of observation shall go toward raising the temperature of any of the fixed parts of the calorimeter. It is evident that if a calorimeter is so constructed that any considerable mass of material, such as a metal chimney, is heated to a fairly high temperature during the operation of the calorimeter, the time required to attain equilibrium will be long. It is not true, as has frequently been supposed, that a large water content *necessarily* means that the calorimeter will require a long time to come to equilibrium, or will be slow in indicating changes in the heating value of the gas tested. A calorimeter of large water content will be slow in showing the effect at the outlet of changes in the temperature of the inlet water, or in coming to equilibrium if it initially contains water the temperature of which differs from that of the inlet water, the lag

being directly proportional to the water content and inversely proportional to the rate of flow of water. A method of reducing errors due to change in temperature of the inlet water is referred to on page 45.

To reduce to a minimum the time lag due to the fixed parts of a calorimeter, it is necessary that all parts which come in contact with the flame or with the heated products of combustion should be made of light material of high thermal conductivity and should be in intimate contact with the water flowing through the calorimeter. If the combustion chamber is made of sheet metal, one side of which is in contact with the water flowing through the instrument, the lag will be small (*a*) because the mass of metal to be heated is small, and (*b*) because the rise in temperature of this metal will also be small. If, however, the combustion chamber consists of heavy metal parts, as in the Boys and Simmance-Abady (American type) calorimeters, and the heat must be transferred from this metal to the water flowing in a pipe in poor thermal contact with these parts, a considerable quantity of heat will be absorbed by the metal before equilibrium is attained, and the lag will be correspondingly great. Insulating material which is slowly heated during the operation of the calorimeter will also increase the time required to attain thermal equilibrium. No indication was found that the use of radiation shields increased the time lag of any of the calorimeters tested.

While the accuracy attainable with a calorimeter of large time lag, under the most favorable conditions, is not necessarily less than that attainable with one of smaller time lag, the former will be very much less convenient and the results obtained with it in ordinary testing are subject to larger errors. The Junkers, Sargent, and Hinman-Junkers are examples of calorimeters of small time lag, while the Boys and Simmance-Abady (American type) represent a type having large time lag.

A convenient method of determining the time lag, is as follows: After the calorimeter has been in operation, i. e., with gas burning and water flowing at the usual rate (the inlet water being kept at constant temperature) until equilibrium has been established, the gas is shut off and the outlet-water thermometer read at frequent intervals until equilibrium is again established. In

Fig. 18 are shown, for different calorimeters, a number of curves which indicate graphically the results of such tests and the relative time lags of the various instruments. In these curves the portions corresponding to the first 8° C of temperature change, after shutting off the gas, have been omitted, so that the curves could be drawn to a more open scale. The form of curve found, for a given calorimeter, obviously may depend upon the rate of water flow and upon the rise in temperature of the outlet water at the time the gas was shut off.

When heating values are to be measured sufficient time should be allowed to elapse after lighting the burner and placing it in position within the calorimeter for the latter to come to an equilibrium condition in all its parts, before beginning observations. From the data represented graphically in Fig. 18, the conclusion was reached that with the Junkers calorimeter, observations may be begun three minutes after placing the lighted burner in position, without incurring risk of making an error exceeding 0.3 per cent due to the lag of the calorimeter. If a sudden change in the character of the gas or its rate of flow is such as to produce a total change in the outlet temperature of 2° F, it will take about 0.8 minutes for 0.9 of this change to take place and about 1.3 minutes for 0.95 to take place, i. e., the error that would result if observations were taken 1.3 minutes after such a change would be 0°.1 F, corresponding to an error of 0.7 per cent in the heating value (i. e., for a 15° F temperature difference). With the Boys calorimeter, under similar conditions, it would take about 10 minutes for 0.9 of the change to take place and about 15 minutes for 0.95 to take place, i. e., before the resulting error in heating value would be reduced to 0.7 per cent. To reduce the source of error under discussion below 0.5 per cent with the Boys calorimeter, the calorimeter should be placed over the lighted burner and fairly steady conditions should persist for 20 minutes before beginning observations. The lag of this calorimeter, as deduced from observations of the rate of cooling, may be somewhat greater than the lag corresponding to the heating up of the calorimeter, as was indicated by an examination of observations made under both conditions. The lag on heating up can not of course be as precisely determined as can the lag on cooling. The

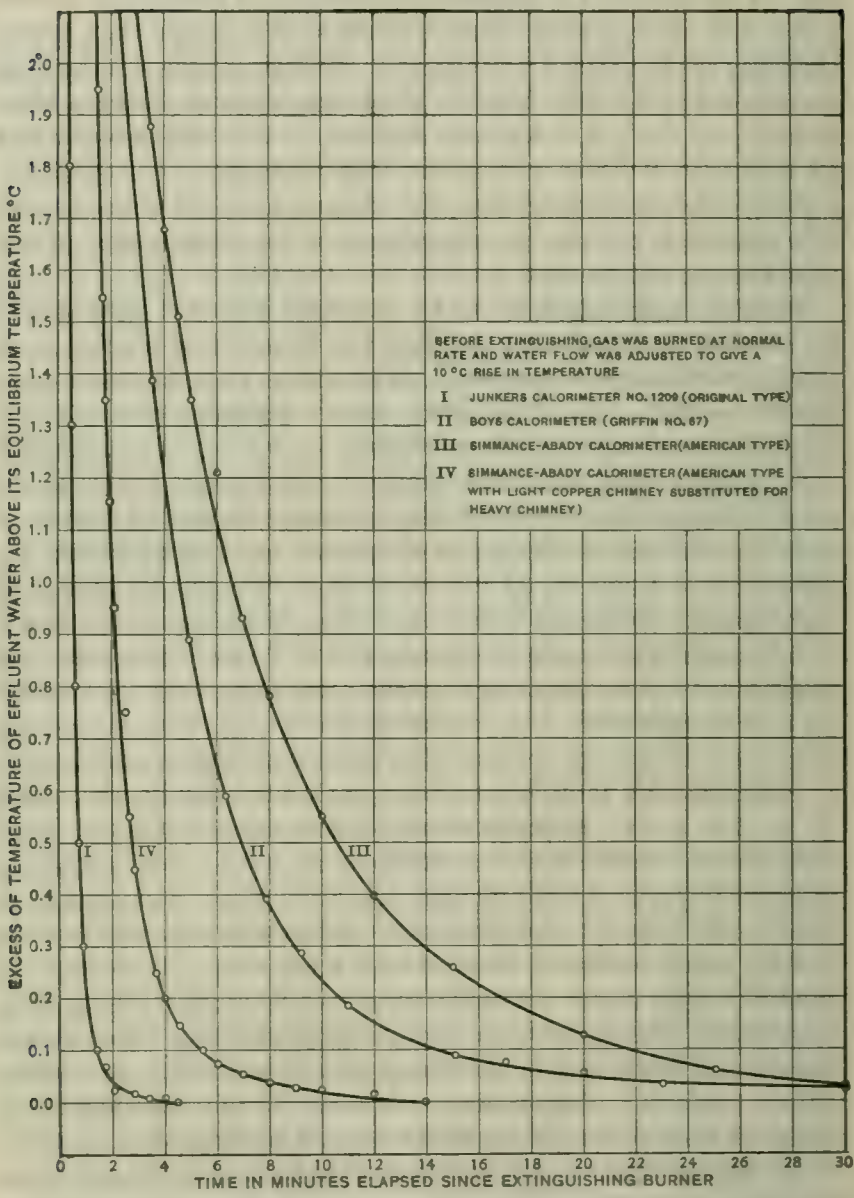


Fig. 18.—*Temperature-time curves for several calorimeters, showing the times required for attainment of thermal equilibrium after extinguishing burner*

statement made above for the Junkers would hold approximately for the Hinman-Junkers and Sargent calorimeters. The Simmance-Abady (American type) calorimeter should be allowed an even longer time than the Boys calorimeter to attain a steady state, before beginning observations, on account of the heavy metal chimney surrounding the burner and in contact with the metal base of the calorimeter.

7. MEASUREMENT OF WATER CONDENSED IN CALORIMETER—NET HEATING VALUE

For the accurate measurement of the amount of water condensed in the calorimeter per unit volume of gas burned, it is essential: (*a*) that there should be no leakage of the water flowing through the calorimeter into the spaces where the water formed in combustion is condensed and collected; (*b*) that the drainage of the condensed water should be uniform. If there are any leaks in the flues, etc., accurate determinations of net heating values are impossible. Uniformity of drainage is promoted by: (*a*) proper shaping of surfaces and ends of tubes, etc; (*b*) uniform wetting of the surfaces. The calorimeter should be operated for a sufficient length of time, before beginning measurements, for the surfaces to become wetted and the drainage therefrom to become uniform. The drainage should not take place from a water surface of large area, as very slight variations in the height of such a surface due to capillarity may cause irregularities in the amount of water collected.

It was found that in a properly designed calorimeter, the amount of water condensed (about 20 cc) during the combustion of a cubic foot of gas did not vary more than about 0.5 cc, in a series of six successive experiments. While at times the error may be somewhat larger than 0.5 cc, it will rarely be necessary to collect the condensate resulting from the combustion of more than a cubic foot of gas, as an error of 1 cc in the amount collected would result in an error of only 2.3 Btu in the net heating value. The amount collected during the combustion of 1 cubic foot of gas is sufficient to render negligible the irregularity due to the fact that the condensed water is discharged in drops (which are rarely larger than 0.1 cc) instead of in a continuous stream. A 25 cc

graduate is suitable for the collection and measurement of the condensed water.

The condensate collected during the time that the meter makes a given number of revolutions corresponds to a certain volume of gas measured under the prevailing conditions of temperature and pressure, etc. If the gas volumes are corrected to standard conditions, the amount of condensate collected must be divided by the same factor used in reducing gas volumes, to find the amount condensed per cubic foot of gas measured under standard conditions. The net heating value is then obtained by subtracting from the observed heating value, the heat of vaporization of the condensed water, and applying other necessary corrections (for heat interchange).

Heat of Vaporization of Water.—The heat of vaporization of water at the temperatures at which calorimetric experiments are usually performed is approximately 2.3 Btu per cubic centimeter or per gram (the difference between expressing the amount in cubic centimeters or in grams being negligible). The constant often used, 2.4 Btu per cubic centimeter corresponds more nearly to the heat of vaporization at 32° F. Since the temperature coefficients of the reactions occurring in combustion are neglected, it is undesirable to use for the heat of vaporization a value not applicable to the temperature of the experiment. The value 2.3 Btu per cubic centimeter should therefore be used for the heat of vaporization of water in the reduction of observations made with flow calorimeters under ordinary conditions.

8. MANIPULATION OF CHANGE-OVER DEVICE

The precision attained in operating the change-over device so as to divert the water from drain to weighing bucket and vice versa at the exact instant the meter index passed through the zero position was tested as follows:

The change-over device (in this case a split funnel mounted on a rotating arm between two stops) was made to operate an electric contact device in circuit with a chronograph. At the instant of passage of the hand of a stop watch through its zero position, as estimated by the operator, he shifted the change-over device, thus causing the time of shifting to be registered by the chronograph.

When the hand of the stop watch again passed through its zero position, the change-over device was shifted back, the exact time of which operation was again registered by the chronograph.

The interval of time that actually elapsed between the operations of shifting the change-over device over and back again was thus found not to differ on the average from the interval the operator had intended to include between these two manipulations by as much as 0.2 second, the difference only occasionally attaining 0.5 second. The error in judging the time of coincidences between index and graduation is probably smaller for the meter (7-inch dial) than for the stop watch (1.5-inch dial). The magnitude of the error that may be caused in a calorimetric determination, due to error in manipulation of the change-over device, may be seen from the following considerations:

If a flow calorimeter is used, in which gas is burned at the rate of 6 cubic feet per hour, and 0.2 cubic foot of gas is burned in a test, the time that elapses between the two operations of shifting the change-over device from drain to bucket and back again is 120 seconds, and as the time interval may be in error by 0.5 second, the corresponding error in the amount of water collected, and hence in the resulting heating value, for any individual determination may attain about 0.4 per cent, although on the average it would be less than half that amount.

The figures given above for the errors of manipulation of the change-over device, dependent as they are upon a number of factors such as the variation in the reaction time of the operator, his skill and experience in such manipulations, etc., would undoubtedly vary with different observers, with the rate of motion of the meter index, with the care taken to avoid parallax, etc. The data given are, however, sufficient to show that the error introduced into a heating value determination by the errors incident to manipulation of the change-over device are no greater than unavoidable errors made in other operations involved in the determination. It is evident that no systematic error is likely to be introduced, unless the two operations of shifting from drain to weighing bucket, and back from bucket to drain, require considerably different manipulation.

The Sargent calorimeter is provided with an automatic change-over device (Fig. 23), the meter index closing an electric circuit when passing through its zero position, thereby energizing an electromagnet, the armature of which is arranged so as to release a dumping bucket. When properly made, such a device reduces the error in the time of shifting to a negligible amount. The contact device must be so made as not to interfere with the proper operation of the meter.

9. WEIGHING OR MEASURING THE WATER

No appreciable error need be introduced in weighing or measuring the water. A Rueprecht 15-kg balance was used in these tests. It was considerably more sensitive than required for the work. A convenient type of balance used with these calorimeters is shown in Fig. 22. The balance is in equilibrium with the empty calorimeter pail in position as one pan of the balance. With such balances weighings can be conveniently and quickly made to an accuracy of a few thousandths of a pound, which is in excess of the required accuracy, as the amount of water to be weighed is usually over 6 pounds.

It is best to have the weights standardized before use. The balance should be tested at occasional intervals for equality of arms by interchange of weights on the balance pans. In a properly designed and well-made balance shifting the position of the weights on the pan should cause no significant change in balance.

In work of high precision with the bomb calorimeter it is customary to reduce all weighings to weight in vacuo. In reducing the observed weight of water to weight in vacuo the observed weight would be increased by approximately 0.1 per cent. This correction can therefore be neglected in gas calorimetry. The correction, however, has been applied in these tests partly from force of habit and partly on the principle of taking into consideration all corrections amounting to 0.1 per cent.

It is good practice to wipe dry the inner wall of the weighing bucket at the conclusion of one test and before beginning the next. However, if the water is simply poured out and the can shaken vigorously while in an inverted position, the amount of water that will remain clinging to the walls will not exceed 1 gram (0.002 pound) for a can with bright tinned inner surface and 3

grams for an oxidized copper or laquered inner surface, corresponding in the worst case cited to an error of 0.1 per cent in the observed heating value.

The small corrections for variation in the specific heat of water with temperature are considered on page 11.

Some calorimeters are furnished with glass graduates for measuring the volume of water instead of weighing it. Such graduates are sometimes made in the form shown in Fig. 30, having an enlargement at the bottom and with only the upper cylindrical portion graduated, thus giving a more open scale in the region actually used without unduly increasing the length of the graduate. If such graduates are carefully standardized, volumes can be readily measured in this way to within 0.1 per cent.

To allow for the combined effects of the variation with temperature of the specific heat of water (for a temperature rise of 15° to 20° F) and the thermal expansion of the water and of the graduate, the observed volumes should be multiplied by the factors K, for temperatures T, as given in Table 22, where T is the temperature of the outlet water, in order to obtain the equivalent mass of water at 15° C (or at 60° F). An additional correction must be applied if the volume of the graduate at 60° F is in error.

TABLE 22

Factors for Reduction of Volumes of Water Measured at T° to Equivalent Mass of Water at 15° C (or at 60° F)

[Multiply observed volume by factor K]

T	K	T	K
°F		°C	
60	1.001	15	1.001
70	0.998	20	0.998
[illegible]	.995	25	.996
90	.993	30	.994
100	.991	35	.992
110	.989	40	.991
		45	.989

It will be seen that, when volumes are measured and the temperature of the outlet water is high, this correction is too large to be neglected.

Evaporation of Water.—The error due to loss of water by evaporation between the time the water leaves the calorimeter and the time the weighing or measuring is done was found to be always negligible. Water may be lost by evaporation, either while the water is flowing from the calorimeter into the measuring vessel or by evaporation from the surface of the water in the vessel. The amount lost while the water was flowing could not be directly measured, but was estimated from thermal data, as follows:

The calorimeter was operated in the usual way, so that the average temperature of the outlet water was about 100° F, the room temperature being 82° and the humidity 63 per cent. The average reading of the outlet-water thermometer during the two minutes that the water was flowing into the weighing bucket was determined, and the temperature of the water in the bucket determined immediately afterwards with the same thermometer. After correcting for the loss of heat from the bucket and for the heat required to raise the temperature of the bucket the total decrease in temperature of the water was found to be less than 0.3° F. The evaporation of 0.1 per cent of the water would lower the temperature of the remainder by about 1° F if all the heat required for evaporation were supplied by the water. The loss of weight by evaporation under the conditions of the experiment, while the water was flowing, was therefore certainly less than 0.03 per cent. Under conditions of lower relative humidity the evaporation might be two or three times as much for the same temperature, but would hardly ever amount to 0.1 per cent. The amount of evaporation will depend upon the change-over device, etc., in use and could readily have been diminished if necessary. The loss of weight by evaporation from the weighing bucket was found, by a series of weighings extending over several hours, to be entirely negligible in the time required for a test.

10. MEASUREMENT OF VOLUME OF GAS

The sources of error that may affect the measurement, by means of wet meters, of the volume of gas burned in a calorimetric test, the precautions to be observed in the use of these meters, and the accuracy attainable in their standardization and use, have been considered in detail in Section VI, relating to "Measurement of the gas volumes," page 23.

11. LEAKAGE OF GAS

The gas meter and the gas connections between the meter and the burner must be free from leaks, and tests for leakage should be made at frequent intervals. The test may be conveniently made, if there is a stopcock at the inlet of the burner, by closing this cock with the gas pressure on, and noting whether there is any appreciable movement of the meter index during an interval of 5 or 10 minutes. If there is no stopcock, the tubing may be disconnected from the burner and a plug inserted in the end of the tube, and the test made as above. The possibility of a leak beyond the point at which the gas is shut off should not be overlooked. The leakage should be made so small that its amount, in the time required for a test, is entirely negligible (less than 0.0001 cubic foot if 0.2 cubic foot of gas is burned in the test). The gas pressure should not be left on the meter except when operating the calorimeter, or when making a leakage test, since so doing may cause a leakage of water through the stuffing box of the drum shaft, which would result in lowering the water level in the meter, thus necessitating more frequent readjustment of the water level.

12. MEASUREMENT OF ATMOSPHERIC PRESSURE

An error of 0.1 inch in the barometer reading will cause an error of 0.3 per cent in the calculated heating value. A barometer should therefore be used, the readings of which are reliable to 0.02 or 0.03 inch. Since the density of mercury and the length of the barometer scale are both affected by the temperature, it is necessary to reduce observed barometer readings to standard conditions; i. e., to the height in inches of the mercury column if the mercury were at 32° F (0° C). Tables for making such reductions, which take into account the variation in length of the scale of the barometer and the variation in the density of mercury with temperature, are readily obtained. The thermometer used for determining the mean temperature of the barometric column is usually mounted on the barometer. The error in heating value due to neglecting entirely the temperature correction of the barometer may attain 0.6 per cent (at a temperature of 95° F). In addition to the temperature corrections, it may be necessary to correct the observed barometer readings to allow for the effects of

(*a*) depression of meniscus if barometer tube is of small bore;[18] (*b*) pressure of any gas that may be above barometric column;[19] (*c*) index error and scale error;[20] (*d*) variation from standard gravity.[21]

If the laboratory has a fairly constant temperature (within 10° F) throughout the year, the total correction to be applied to the barometric readings, to allow for the combined effects of all the corrections mentioned above, may be determined once for all, either by evaluation of the individual corrections, or more conveniently, by comparison with a standardized barometer. Under these circumstances, a pressure regulator may be connected between the gas supply and the meter and the inlet pressure on the meter may be adjusted, provided the pressure of the gas supply is always sufficient, so that the excess of pressure in the meter, above atmospheric pressure, is equal and of opposite sign (since the temperature correction is the principal one) to the sum of all the barometric corrections, in which case the pressure of the gas in the meter will be given directly by the reading of the barometer.

For example, the temperature of the laboratory in which the present experiments were made averaged about 82° F, during a considerable part of the year. The total barometric correction for this temperature was −0.15 inches. The inlet pressure on the meter was therefore made equal to 2.1 inches of water, so that the uncorrected barometric reading was equal to the pressure of the gas in the meter. This method of compensating for the

[18] If the bore of the barometer tube is small, the pressure of the mercury meniscus may be sufficient to depress the barometric column by an amount that is significant. Thus in a tube of one-fourth inch bore, the depression may attain 0.05 inch. This source of error may be oviated by avoiding the use of a barometer tube of bore as small as one-fourth inch. The meniscus correction is discussed in Bureau of Standards Circular No. 46.

[19] In a barometer that has been filled with proper care, the trace of air above the mercury column should be so small as to exert no significant pressure. In most barometers the presence of air can only be detected by comparisons with a standard barometer at various pressures. In a primary standard barometer the effect of residual gas can be determined by measuring the same pressure with the upper mercury meniscus at different parts of the tube.

[20] In a barometer in which the position of the lower mercury surface is fixed by an index, the setting of the index, with reference to the graduated scale may be in error, in which case a correction for index error is necessary.

[21] Since gravity varies from place to place and with the altitude of the station, the pressure exerted by a barometric column of specified height will also vary. This correction varies from practically zero in the most northern latitude of the United States to about 1 part in 600 of the observed barometric height in the most southern latitude. The correction for variation of gravity with altitude is entirely negligible in gas calorimetric measurements.

barometric corrections is evidently not applicable if the sum of these corrections has a too small negative, or a positive value.

13. EFFECT OF USING FRESH WATER IN GAS METER

It is well known that water will absorb in different degrees the various constituent gases that enter into the composition of illuminating gas. The rate of absorption will evidently depend upon the degree of saturation of the water by each constituent, being greater if the water is fresh. The effect of absorption manifests itself in two ways: (*a*) in causing an error in the measurement of volume; (*b*) in changing the heating value of the complex mixture by selective absorption, so that the composition of the gas delivered, after passage through the meter, is different from that entering the meter. An idea of the magnitude of the effect is given by the results in Table 23. The meter having been filled with fresh water, the observed heating values recorded in column 3 were found after the amounts of gas recorded in column 2 had passed through the meter.

TABLE 23

Effect of Use of Fresh Water in Meter on Observed Heating Value

[Junkers calorimeter No. 1209. Gas rate=5.5 cubic feet per hour]

Time	Volume gas passed through meter since filling with fresh water	Observed heating value of gas
h. m.	cu. ft.	Btu.
4 13	0.5	555
4 16	0.8	657
4 24	1.5	659
4 27	1.8	658
4 46	3.5	659
4 49	3.8	660
5 02	4.9	659
5 05	5.2	659

It will be seen that the effect, due to the use of fresh water in the meter, on the observed heating value of this sample of illuminating gas was of the order of 0.5 per cent and that the water had become practically saturated, so far as calorimetric measure-

ments are concerned, after the passage of 2 or 3 cubic feet of the gas.

An experiment was arranged to determine directly the effect of any possible absorption of the constituents of the gas by fresh water. For this purpose two meters were joined in series, one being filled with water saturated with the gas, the other with fresh water. The water in both meters was at room temperature. The ratios of the volumes of gas indicated by the two meters was then determined immediately after the gas was first turned on and at intervals thereafter until about 10 cubic feet had been passed. To determine whether the fresh water was still absorbing gas, the gas was then passed through the meters in the opposite direction and the same value was found for the ratio of volumes indicated by the two meters. These experiments showed that the absorption of gas in the meter filled with fresh water did not exceed 0.2 per cent, even at the start when only a half cubic foot of gas had been passed through the meters. The same result was found in two such experiments, in one of which the gas was passed first through the meter containing the fresh water and in the other of which the gas was passed first through the meter containing the saturated water.

Any effect on the observed heating value due to absorption of gas by the water in the meter may, therefore, be avoided by running several cubic feet of gas through the meter, after filling it with fresh water.

14. EFFECT OF USE OF NEW RUBBER TUBING

It is known that the absorption of constituents of illuminating gas by rubber tubing through which the gas is passed may cause a measurable change in its properties. To accentuate any such effect, an experiment was arranged as follows: Gas from the holder was led to the meter through a short length of rubber tubing. From the meter the gas was passed to the regulator and thence to the burner through either of two circuits, in one of which was about 5 feet of old rubber tubing that had long been in contact with gas, while in the other circuit a 33-foot length of new rubber tubing, which had never been in contact with gas, was included. A series of heating value determinations was then made from time

to time with the gas taken alternately through these two circuits. The results of these experiments are shown by the curves, Fig. 19. It will be seen that the 33-foot length of new tubing lowered the observed heating value, during the first few minutes, by about 2 per cent. After 29 hours the observed heating value of the gas was still about 0.5 per cent lower than when passed through the old tubing. The effect was not due to leakage in the ordinary sense; i. e., when the gas was shut off at the burner, observation of the meter indicated that there was no appreciable leakage. The precaution to be observed to eliminate this source of error is to use tubing thoroughly saturated with the gas, and as only 4 or 5 feet of tubing, or much less in a permanent installation, are necessary,

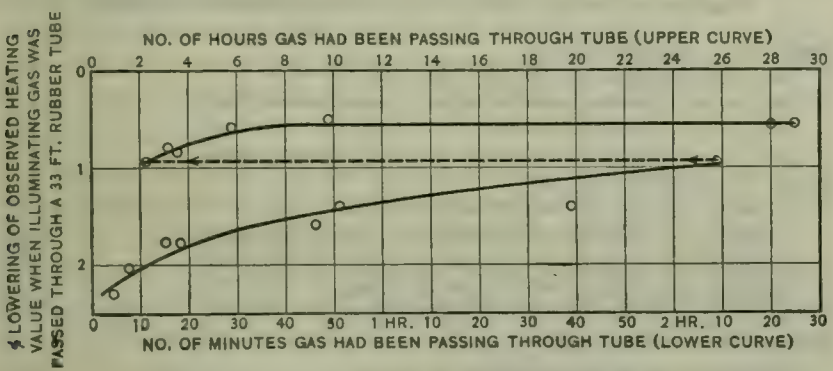

NO. OF HOURS GAS HAD BEEN PASSING THROUGH TUBE (UPPER CURVE)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
0
1
2
% LOWERING OF OBSERVED HEATING VALUE WHEN ILLUMINATING GAS WAS PASSED THROUGH A 33 FT. RUBBER TUBE
0 10 20 30 40 50 1 HR. 10 20 30 40 50 2 HR. 10 20 30
NO. OF MINUTES GAS HAD BEEN PASSING THROUGH TUBE (LOWER CURVE)

Fig. 19.—*Effect of new rubber tubing on heating value*

the effect will be negligible after the tubing has been in contact with the gas for several hours.

15. EFFECT OF COOLING GAS ON HEATING VALUE AND ON CANDLEPOWER

Alternate tests were made of the heating value of illuminating gas as drawn directly from the holder and as drawn through a copper coil immersed in melting ice. The decrease in the observed heating value due to lowering the temperature (for a brief interval) to nearly 32° F was 0.7 per cent. Similar experiments on the candlepower showed a decrease in candlepower of nearly 12 per cent. These experiments were made in the early autumn so that the gas had not been previously exposed to low temperatures in the mains. That the effect of exposure of oil-enriched illuminating

gases to low temperatures results in a far greater change in their candlepowers than in their heating values is so well known that further experiments along this line seemed unnecessary for the purposes of this investigation, the important point being merely to draw attention to the occurrence of such changes.

16. DETERIORATION IN HEATING VALUE OF GAS IN HOLDER

The data summarized in Table 24 show that the illuminating gas used in these experiments deteriorated in heating value when allowed to stand in contact with water in the 5 cubic foot holder.

TABLE 24

Change in Heating Value of Gas During Storage in Holder

Sample No. 1, illuminating gas:
July 30, 1913, gas holder filled at 9.30 a. m.
July 30, 1913, heating value found at 11.30 a. m.=660 Btu.
July 30, 1913, heating value found at 3.45 p. m.=661 Btu.
July 31, 1913, heating value found at 4.15 p. m.=653 Btu.
Sample No. 2, illuminating gas:
August 1, 1913, gas holder filled at 10.36 a. m.
August 1, 1913, heating value found at 10.45 a. m.=661 Btu.
August 1, 1913, heating value found at 4.00 p. m.=661 Btu.
August 2, 1913, heating value found at 1.00 p. m.=657 Btu.
August 4, 1913, heating value found at 11.00 a. m.=648 Btu.
Sample No. 3, illuminating gas:
August 4, 1913, gas holder filled at 2 p. m.
August 7, 1913, heating value found at 10.30 a. m.=658 Btu.
August 7, 1913, heating value found at 4.00 p. m.=659 Btu.
August 8, 1913, heating value found at 9.30 a. m.=654 Btu.

It will be seen that the deterioration amounted to 2 per cent in the course of several days. The magnitude of this effect would probably be different for gases of very different composition. It might also be expected that the rate of change might be different with a holder in which the area in contact with the water was different. It is therefore evident that if the object in view is the determination of the heating value of the sample of gas when drawn from the mains, the sample should be tested shortly after the gas holder is filled, or if the gas is stored for some time before testing, the effect of storage under the prevailing conditions should be investigated.

17. RÉSUMÉ OF FACTORS AFFECTING HEATING VALUE DETERMINATIONS

The foregoing discussion of the errors that may affect the various measurements and manipulations incident to the determination of heating values with flow calorimeters may, at first sight, seem rather formidable and leave the impression that the final accuracy of such determinations may not be as high as is desirable or even as is required in industrial testing. However, experience has shown that, if due attention is given to the precautions that have been shown to be of importance, an accuracy better than 0.5 per cent is attainable, and in ordinary routine testing an experienced observer should obtain results accurate to within about 1 per cent.

Thus it has been shown:

1. There is little probability of error due to incomplete combustion if the calorimeter is not operated at too high a rate of gas consumption.

2. Care is necessary in measuring the rise of temperature of the water; standardized thermometers should be used and the thermometer corrections and stem corrections should be applied.

3. If the calorimeter is operated with the inlet water at room temperature, if the burner is provided with radiation shields and is properly mounted within the calorimeter, if the calorimeter is operated at the normal rate and the correction for effect of atmospheric humidity is applied, the remaining heat losses will, for most calorimeters, introduce no significant error, while, if such losses are significant for the calorimeter used, a correction may be applied.

4. If the inlet water is not at room temperature the corrections necessary on this account may be readily applied.

5. The flow of water and of gas can readily be made sufficiently constant.

6. By waiting until the calorimeter is in thermal equilibrium (from 5 to 30 minutes, depending on the calorimeter used) no significant error due to its lag will be introduced unless there are considerable variations in the heating value of the gas being tested, in the rate of flow of gas or water, etc.

7. With a properly designed calorimeter, the drainage from which is uniform, the measurement of the condensed water offers no difficulty.

8. Care is necessary in manipulating the change-over device, since large accidental errors may be introduced in this operation, although no significant constant error need be introduced.

9. The weighing or measuring of the water with sufficient accuracy presents no difficulties.

10. Great care must be exercised in calibrating the gas meter and in making the necessary adjustments in its subsequent use. The other operations incidental to the measurement of gas volumes need introduce no significant error.

11. If tests are made regularly for leakage of gas, the effects of leakage may easily be reduced to negligible proportions.

12. With a standardized mercury barometer, the accuracy required in gas testing is easily attainable.

13–16. Errors may be introduced on account of changes in the character of the gas, due to various influences, the effect of which, however, may be easily avoided.

It appears therefore that the accuracy attainable in heating value determinations with flow calorimeters is mainly limited by errors in adjusting the gas meter, in measuring the temperature rise of the water, and in manipulating the change-over device, since the errors due to other factors may, by proper procedure, be made nearly, if not quite, negligible.

VIII. COMPARISON OF HEATING VALUES OF GASES DETERMINED WITH FLOW CALORIMETERS WITH THOSE OBTAINED WITH CALORIMETERS OF THE BERTHELOT BOMB TYPE

1. APPARATUS AND METHODS

In order to obtain a check on the accuracy of determinations of the total heats of combustion of gases, as made with industrial flow calorimeters, several gases having quite different heating values, viz, a natural gas, an oil enriched illuminating gas and nearly pure hydrogen were burned in a Junkers and in a Hinman-Junkers calorimeter of the flow type, and in a Williams and in a Kroeker-Peters calorimeter of the Berthelot bomb type. In

calorimeters of the bomb type the combustion takes place at constant volume. A suitable correction was therefore applied (dependent upon the change of volume occurring in combustion at constant pressure) to reduce the results obtained with the bombs to the corresponding values at constant pressure. The Williams bomb was provided with a gold lining; the Kroeker-Peters bomb with an enamel lining. The bombs were used in a specially designed calorimeter in an inclosure surrounded on all sides by a constant temperature water jacket. The temperature changes of the calorimeter were measured by means of a calorimetric platinum resistance thermometer and a special Wheatstone resistance bridge capable of measuring small temperature changes to one or two ten-thousandths of a degree. The entire calorimetric equipment has been in use at the laboratories of the Bureau for several years in an extended series of researches and full details will be published in subsequent communications.

The internal volumes of the bombs were determined in the following manner: The bomb, immersed in a water bath at known temperature, was nearly filled with freshly boiled distilled water; the bomb was then exhausted by a motor driven Geryk pump and the water thus boiled at reduced pressure to expel all traces of air remaining in the bomb; distilled water was then run into the bomb to completely fill it. From the mass of water required to completely fill the bomb, the volumes of the Williams and of the Kroeker-Peters bombs were found to be 606.1 cc and 266.6 cc, respectively, at 28° C.

The bomb, containing 0.5 cc of water, was connected by means of a three-way stopcock, alternately to a vacuum system, in which the pressure was about 0.1 atmosphere, and to the supply of gas, the heat of combustion of which was to be determined. The gas was drawn from the gas holder, at a pressure of a few inches of water above atmospheric, and was in equilibrium with water, so that the gas was practically saturated with water vapor at room temperature.

To insure that the gas in the bomb was saturated with water vapor at the known temperature of the bath, the bomb, after being alternately evacuated and filled with the gas a number of times, was immersed for some minutes in a water bath the tem-

perature (usually about 100°–110° F) of which was considerably above that of the room, was again evacuated and again connected to the gas supply. This precaution was really unnecessary, as was shown by the results of a number of experiments in which it was omitted. The bomb was then transferred to a thermostatic water bath at room temperature and after taking up the temperature of this bath, was momentarily opened to the air, through the three-way stopcock, which in the meantime had been disconnected from the vacuum system. The valve of the bomb was then closed. Diffusion of air into the bomb, while it was open to the atmosphere, was prevented by the fact that the connection between the interior of the bomb and the atmosphere was through a narrow tube filled with the same gas as that contained in the bomb. The volume of saturated gas contained in the bomb was equal to the volume of the bomb as determined above, the pressure of the gas being equal to the atmospheric pressure at the instant the valve was closed, and the temperature being that of the water bath in which the bomb was immersed.

Oxygen (95+ per cent, with the residue mainly argon), in excess of that required for complete combustion of the contained gas, was then run into the bomb, the amount being calculated from the indications of a calibrated closed end mercury manometer connected to the oxygen supply piping.

The bomb was then placed in the calorimeter, and after a suitable series of temperature observations to obtain the rate of rise of temperature during the preperiod, the mixture of gas and oxygen was fired, at a given time, by heating momentarily to incandescence a short length (a few mm) of 0.05 mm platinum wire between the electrodes within the bomb, by means of current from a 2-volt storage cell in series with a suitable resistance. The energy thus supplied by the firing current was absolutely negligible. Temperature observations were then continued during the so-called middle and after periods, from which observations was deduced the temperature rise, corrected for gain or loss of heat from the surroundings. The water equivalents of the calorimeters (including bomb, can, stirrer, thermometer, and water) had been carefully determined in previous investigations by a method of elec-

trical standardization. These data were again checked by H. G. Barrott by burning in the calorimeter standard combustion samples of benzoic acid; the agreement between the water equivalent thus determined and the older data was of the order of 1 part in 1000.

After the conclusion of each gas combustion, the interior of the bomb was washed with distilled water and the washings were titrated with a one-tenth normal solution of NaOH. As the oxygen used contained but a trace of nitrogen, the correction thus determined for the nitric acid formed in the combustion, and for any sulphuric acid resulting from traces of sulphur in the gas, was so small that it could have been entirely neglected, never exceeding 1 part in 1200 of the heat involved in the combustion.

2. COMPARISONS WITH NATURAL GAS

The results of determinations of the heating value of a sample of natural gas from the fields near Independence, Kans., as carried out with the Junkers and with the Hinman-Junkers flow calorimeters and with the Williams and with the Kroeker-Peters bombs are summarized in Table 25. The gas had been filled into a 5 cubic-foot steel cylinder from the discharge line of a compressor at a pressure of 250 pounds per square inch. For this sample of natural gas the Bureau is indebted to Messrs. A. B. Macbeth and J. B. Klumpp.

As will be seen from Table 25, the experimental conditions for the tests with the flow calorimeters were varied in many ways to obtain a check on the reliability of the results. Different calorimeters were used; the rate of gas consumption was varied; inlet and outlet water thermometers were interchanged and different pairs of thermometers were used; different wet meters were used, which were repeatedly calibrated, often both before and after the tests; by varying the air supply the character of the flame was changed from a partly luminous to a strongly oxidizing flame; different Bunsen burners were used, one with several different size tips (2.2, 1.6, 1.1 mm) substituted for the usual 2.2-mm tips used with illuminating gas, and a Méker burner with a 1-mm tip, to give the characteristic Méker flame; the pressure of the gas both

in the meter and at the burner tip was varied, and the gas was burned at different rates. During the experiments the atmospheric humidity varied between 40 per cent and 80 per cent and the temperature between 75° F and 85° F.

TABLE 25

Determinations of Heating Values of a Sample of Natural Gas from Fields near Independence, Kans.

DATA OBTAINED WITH FLOW CALORIMETERS

Date	Series Nos	Humidity	Room temperature	Gas rate	Observed heating value	Net heating value	Total heating value	Remarks
1913		Per cent	°F	Cu. ft. hr.	Btu	Btu	Btu	
June 17	1	49	84	4.0	989	903	997	
18	2	43	82	4.0	990	904	999	
19	4	55	82	4.0	991	903	997	
20	5	62	82	4.0	993	904	998	
20	6	62	82	2.7	989	903	(998)	Total calc. from net.
20	7	62	82	4.7	994	904	(999)	Do.
20	8	62	82	4.0	993	902	998	
23	9	64	80	4.0	996	903	999	
23	11	70	77	4.0	996	904	999	
24	12	71	77	4.0	992	900	995	
25	13	74	80	4.0	996	902	999	Another gas meter in remaining tests.
25	14	78	80	4.0	996	902	998	Excess air in Bunsen.
25	15	78	80	4.0	(987)	.....	.....	Incomplete combustion shown by odor of products.
25	16	78	80	4.0	995	904	999	
26	17	72	80	4.0	994	902	996	Meker burner.
26	18	72	80	4.0	997	903	999	
26	19	73	81	6.5	997	903	999	Damper open.
26	20	78	81	3.0	997	.....	999	Hinman - Junkers Calorimeter No. 164; normal rate.
28	21	53	87	4.0	991	902	998	
28	22	58	86	4.0	992	903	998	Very large excess of air in Bunsen.
July 14	23	49	84	4.0	991	902	1000	
16	25	60	82	4.0	988	902	997	
Mean						903	998	

TABLE 25—Continued

DATA OBTAINED WITH THE WILLIAMS AND THE KROEKER-PETERS BOMB CALORIMETERS

Date	Series No.	Excess oxygen	Liters of saturated gas burned, measured at 28° C. 760 mm	Corrected temperature rise of calorimeter	Heat capacity of calorimeter	Correction for HNO_3 formed	Heat of combustion at constant volume, per liter of saturated gas, measured at 28° C, 760 mm	Heat of combustion at constant pressure, per liter of saturated gas, measured at 28° C, 760 mm
1913		Per cent		°C	15° cal.	calories	calories	calories
June 18	3	13	0.6042	1.6529	3035	−2.1	8299	8347
18	3	16	.6034	1.6497	3035	−1.8	8295	8343
18	3	34	.6033	1.6487	3035	−2.7	8290	8338
18	3	26	.6031	1.6469	3035	−2.7	8283	8331
23	10	16	.6044	1.6537	3035	−2.4	8310	8358
23	10	11	.6037	1.6486	3035	−2.4	8285	8333
July 15	24	20	.2638	0.6415	3410	− .4	8291	8339
15	24	24	.2637	.6415	3410	− .4	8294	8342
15	24	30	.2635	.6405	3410	− .5	8287	8335
Heat of combustion of 1 liter saturated gas, measured at 28° C, 760 mm = 8291 8339								
∴ Total heating value = 1001 Btu per cubic foot								

Each series in Table 25 consisted of from two to four separate determinations. The pressure of the gas in the cylinder at beginning of the series of experiments was 260 pounds per square inch, and this was reduced to 40 pounds per square inch at the end of the experiments.

The results obtained under all these varied conditions were quite consistent. The mean total heating value of the sample of natural gas contained in the cylinder, as determined with the flow calorimeters, was found to be 998 Btu per cubic foot.

The mean total heating value of the same sample of gas, as determined by the bomb calorimeters, was 1001 Btu per cubic foot. The difference between the results found with the two methods of calorimetry is within the limits of the combined effects of experimental errors.

3. COMPARISONS WITH HYDROGEN

Nearly pure hydrogen was burned in the Junkers calorimeter No. 1209 and in the Williams bomb calorimeter. The hydrogen was produced electrolytically from a solution of caustic potash and was collected over water in the 5-cubic-foot gas holder. While the hydrogen was probably of a fair degree of purity, the holder and connections having been washed out several times before the final filling, no attempt was made to purify the gas delivered by the generator, and no analyses of the gas were made, the object in view being not a determination of the heating value of hydrogen but a comparison of results obtained with flow and with bomb calorimeters, respectively, when applied to a gas of low heating value.

A preliminary calculation showed that if the Junkers calorimeter were used with the usual damper furnished with it (two 15-mm openings) the normal rate for hydrogen would be too large to permit of accurate metering. A damper having two 8-mm openings was therefore substituted, and with this damper the normal rate for hydrogen was found to be about 7.3 cubic feet per hour.

The manipulation of the bomb was similar to that in the experiments with natural gas.

The results obtained for the heat of combustion of the nearly pure hydrogen with the Junkers calorimeter and with the Williams bomb calorimeter, together with the more important data relating to these experiments, are summarized in Table 26.

TABLE 26

Determination of Heating Value of a Sample of Nearly Pure Hydrogen

DATA OBTAINED WITH JUNKERS CALORIMETER NO. 1209

Date	Experiment No.	Humidity	Room temperature	Gas rate	Observed heating value	Net heating value	Total heating value
1913		Per cent	°F	Cu ft per hr	Btu	Btu	Btu
Aug. 12	1	55	77	7.3	318.5	269.6	318.6
12	2	55	77	7.3	318.4		318.5
15	6	59	78	7.3	317.4	269.2	317.9
15	7	59	78	7.3	317.5		318.0
Mean						269.4	318.2

TABLE 26—Continued

DATA OBTAINED WITH WILLIAMS BOMB CALORIMETER

Date	Experiment No.	Excess o oxygen	Liters of saturated gas burned, measured at 28° C, 760 mm	Corrected temperature rise of calorimeter	Heat capacity of calorimeter	Correction for HNO_3 formed	Heat of combustion at constant volume, per liter of saturated gas, measured at 28° C, 760 mm	Heat of combustion at constant pressure, per liter of saturated gas, measured at 28° C, 760 mm
1913		Per cent		°C	15° calories	calories	calories	calories
Aug. 14	3	50	0.6005	0.5166	3035	−1.7	2608	2644
14	4	90	.6006	.5174	3035	−1.8	2612	2648
14	5	130	.6005	.5181	3035	−2.5	2614	2650
Heat of combustion of 1 liter saturated gas, measured at 28° C, 760 mm=							.....	2647
∴ Total heating value=317.6 Btu per cubic foot								

4. COMPARISONS WITH ILLUMINATING GAS

With gases like hydrogen or like natural gas, which are quite stable in character, the results found for the total heating value by the flow calorimeter method were in excellent agreement with the results found by the calorimetric bomb method. The results obtained, however, in comparing these methods when an oil-enriched illuminating gas was used were not satisfactory. A number of tests by the two methods were made which seemed to show that the heating values determined with the bomb were nearly 1 per cent lower than the values found with the Junkers calorimeter. The earlier tests were not all made on the same day, however, and as it had developed from these experiments that the gas standing in the holder in contact with water suffered a progressive deterioration in heating value (see p. 98), another series of tests by the two methods was planned which was completed in one day, the determinations with the two bombs already described being preceded and followed by determinations with the Junkers calorimeter. The details of manipulation were similar to those previously described in connection with the experiments on natural gas. The excess of oxygen in the bombs, over that required for combustion, was varied from 25 per cent to 100 per cent. The heat of combustion obtained with the bombs was again about 1 per cent lower than that found with the flow calorimeter.

This apparent difference in the results found by the two methods is, so far as the evidence at hand shows, not a real one due to the instruments, but is to be attributed to the character of the gas, since when the more stable and homogeneous gases were used no such difference between the results obtained with the two methods was found to exist.

The difference in the results found with the Junkers flow calorimeter and with the bomb calorimeters was attributed to some change in the character of the unstable illuminating gas when allowed to expand into the evacuated bomb. Accordingly, it was decided to fill the bomb by drawing gas through it for some time, i. e., by a method of transpiration instead of by the method of successive evacuations previously used. This method could not, however, be used with the Williams bomb, which had only one inlet. To eliminate the possible effect of selective absorption of the constituents of the gas by the rubber tubing, the latter was replaced by glass tubing. Under these conditions the Kroeker-Peters bomb gave results for illuminating gas about 0.5 per cent higher than were found with the Junkers flow calorimeter.

In view of the marked differences found for the illuminating gas, when used under different conditions in the bomb calorimeter, it was decided to substitute for the unstable illuminating gas a mixed gas of more stable character and having a heating value approximately equal to that of the illuminating gas. This mixed gas was produced in the gas holder by mixing natural gas with hydrogen, produced electrolytically. One set of results found with this mixed gas is summarized below.

It will be seen that the results obtained with the several calorimeters are in satisfactory agreement.

It is not yet clear why the illuminating gas, when filled into the Kroeker-Peters bomb by the method of transpiration, should give results about 0.5 per cent higher than those found with the Junkers calorimeter. In this connection it should be remarked that the Kroeker-Peters bomb gave results a few tenths of a per cent higher than the Williams bomb. The difference may be due to the presence of the enamel lining. Thus, for example, no acidity is detected in the washings of this bomb after a combustion. The

platinum-lined Kroeker-Peters bomb was not used for the reason that the explosion of the gas would be likely to tear loose the platinum lining. If this difference between the two bombs is a real one, the discrepancy above referred to for illuminating gas practically disappears. At any rate the small outstanding discrepancy for the illuminating gas is evidently a problem in bomb calorimetry requiring further investigation and it was not deemed worth while withholding the results of the present investigation awaiting the solution of that problem.

TABLE 27

Heating Value Determinations of Mixed Gas (Natural Gas and Hydrogen) with Junkers Calorimeter No. 1209 and with the Williams Gold-lined Bomb Calorimeter and the Kroeker-Peters Enamel-lined Bomb Calorimeter

Date	Expt. No.	Calorimeter.		
		Junkers	Williams	Kroeker-Peters
July 28, 1914	1	636		
	II	...	[a] 637	
	III	...	....	[a] 637
	IV	...	[a] 636	
	V	...	....	[a] 639
July 29, 1914	6	...	[a] 635	
	7	...	....	[a] 639
	VIII	...	[a] 635	
	9	...	....	[b] 639
	VIII	...	....	[b] 638
	11	636		
Mean		636	636	638

[a] Bomb filled with gas by method of successive evacuation and refilling.
[b] Bomb filled by drawing gas through for long time.

From the agreement of the results found with the Junkers calorimeter and the bomb calorimeters when used with natural gas, with hydrogen, and with the mixed gas it seems safe to conclude that the heating values found by the above two very different methods of calorimetry are in agreement to within the limits of accuracy of the work (a few tenths of 1 per cent).

IX. TESTS OF VARIOUS GAS CALORIMETERS

In this section are summarized the results of such special tests as were made on the several calorimeters listed in Table 1. Many special experiments relating to these calorimeters, and which illustrate the general principles underlying the operation of flow calorimeters, have been described in previous sections of this paper.

The essential details of construction and the principle of action (briefly discussed on p. 17) of the various calorimeters will be readily understood by examination of the photographic reproductions and the sectional drawings of the instruments. Detailed explanations relating thereto, which may be found in trade catalogues and in published papers, have therefore been omitted or reduced to a minimum.

Criticisms have been made here and there which often relate to minor defects of design or construction that are very easily remedied. Such criticisms are in no sense a condemnation of the instrument and they have been made mainly with the object of calling the attention of the user to such defects, so that he may be on the lookout for them. Such minor defects are particularly likely to occur where types have not been standardized as to details of manufacture.

As the Junkers calorimeter No. 1209 had been compared with calorimeters of the Berthelot bomb type, and furthermore, as an exhaustive investigation had been made of the various constants of and heat losses from this calorimeter, it was used to determine the total and net heating values of various samples of gas, simultaneous determinations being made on the same samples of gas with the calorimeter under investigation. The same meter was used throughout such a series of experiments, so that the errors incident to metering were, to a large extent, eliminated from the results.

1. JUNKERS CALORIMETER (ORIGINAL TYPE)

Description.—This calorimeter is illustrated in Figs. 20 and 21. The water from the source of supply enters the inlet overflow wier, passes downward through the tube on the left, through a valve for controlling the rate of flow, past the bulb of the inlet-

Fig. 20

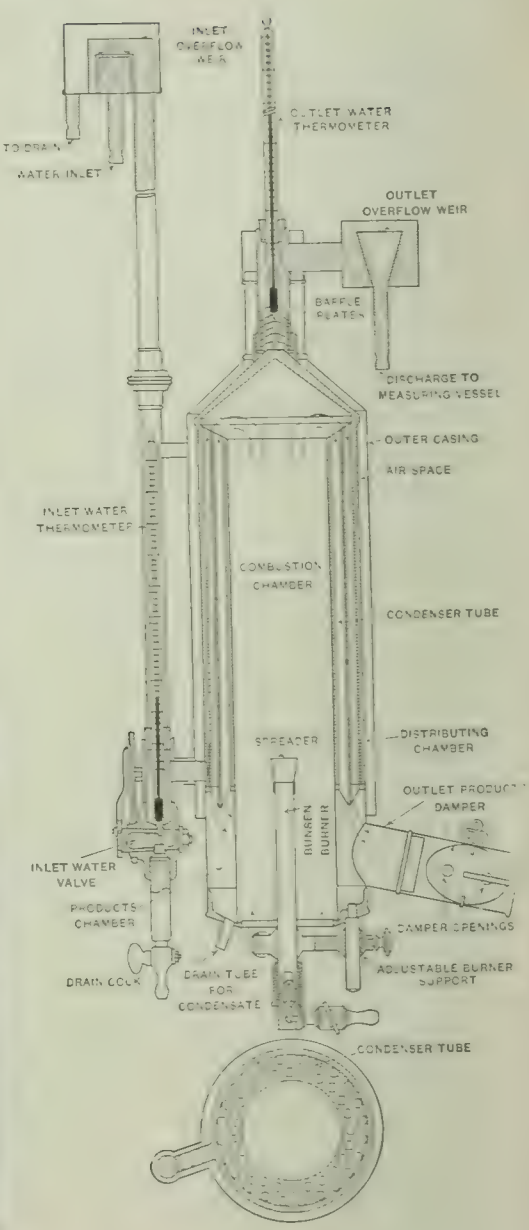


Fig. 21

Junkers calorimeter (original type)

water thermometer and enters a distributing chamber at the bottom of the calorimeter. The water then flows upward over the outside of a set of vertical condenser tubes in the inner annular cylindrical space surrounding the combustion chamber, through the conical space above the combustion chamber and through the small cylindrical space at the top, in which are placed several mixing diaphragms to thoroughly mix the stream of water before it reaches the bulb of the outlet-water thermometer, in order that the latter will assume the true mean temperature of the effluent stream of water, which has taken up the heat from the products of combustion. The water then passes out of the calorimeter, through the short horizontal tube at the top, into the outlet overflow wier, from which it is discharged. The total water content of this calorimeter is somewhat in excess of three pounds.

The gas is burned in a Bunsen burner within the combustion chamber. The products of combustion pass upward to the top of the combustion chamber, then downward through the condenser tubes mentioned above, into the products chamber at the bottom of the calorimeter, and thence are discharged into the air through an outlet tube in which is placed the bulb of the products thermometer and also an adjustable damper. The entire calorimeter, with the exception of the products chamber at the bottom, is inclosed in a concentric nickel-plated casing of thin copper, thus forming an air space between the casing and the calorimeter proper. A small hole at the bottom of the casing permits the escape of any water which may leak into the air space, and thus provides a means of indicating the presence of leaks in those parts of the calorimeter which are inclosed by the outer casing.

The design of this calorimeter has been criticized on account of the inconvenience in reading the inlet- and outlet-water thermometers, which are at different levels. When the inlet water is maintained at constant temperature, so that this temperature has to be read only at the beginning and end of a test, the inconvenience referred to is of little importance. In some of the modifications of this calorimeter to be discussed later, the thermometers are brought to the same level by mounting the inlet-water thermometer in the inlet water pipe, at a greater distance from the

bottom of the calorimeter. However, in the modified calorimeters, the inlet-water thermometer, as well as the inlet water valve in some models, are in the descending stream of water, instead of in the ascending stream, as in the original model, thus increasing the possibility of the formation of air traps, with consequent irregularity in the rate of water flow.

Special Tests.—It was shown on p. 57 that when the burner holder was modified so that the burner could be raised sufficiently to bring the base of the flame about 1.5 inches above the horizontal plane defined by the boundary surface between the bottom of the water chamber and the top of the products chamber at the base of the calorimeter and when radiation shields were used on the burner, reheating of the products in this lower chamber was prevented, so that the products then escaped from the calorimeter at practically the temperature of the inlet water. It was also shown that the use of radiation shields on the burner raised the observed heating value several tenths of 1 per cent.

The combustion chamber is of ample size and the spaces provided for the passage of the products of combustion are of sufficient size to permit of burning illuminating gas at rates up to 15 cubic feet per hour. Experiments made to determine the volume of entering air and of discharged products, for various rates of gas consumption, have been described on p. 64. The damper furnished with the instrument had two 15-mm openings and with this damper closed, the normal rate of gas consumption (defined on p. 69) was about 7 cubic feet per hour for illuminating gas (650 Btu) and about 4 cubic feet per hour for natural gas (1000 Btu).

The calorimeter is so designed and constructed that the drainage therefrom, of the water resulting from the condensation of aqueous vapor from the products of combustion, is regular, so that net heating values can be accurately determined.

The efficiency of the calorimeter as a heat absorber, defined in a somewhat restricted sense as the ratio of the amount of heat absorbed by the water flowing through the calorimeter (product of mass of water, its specific heat and its indicated rise in temperature) to the amount of heat supplied as electric energy to an electric heating coil in the combustion chamber, has been con-

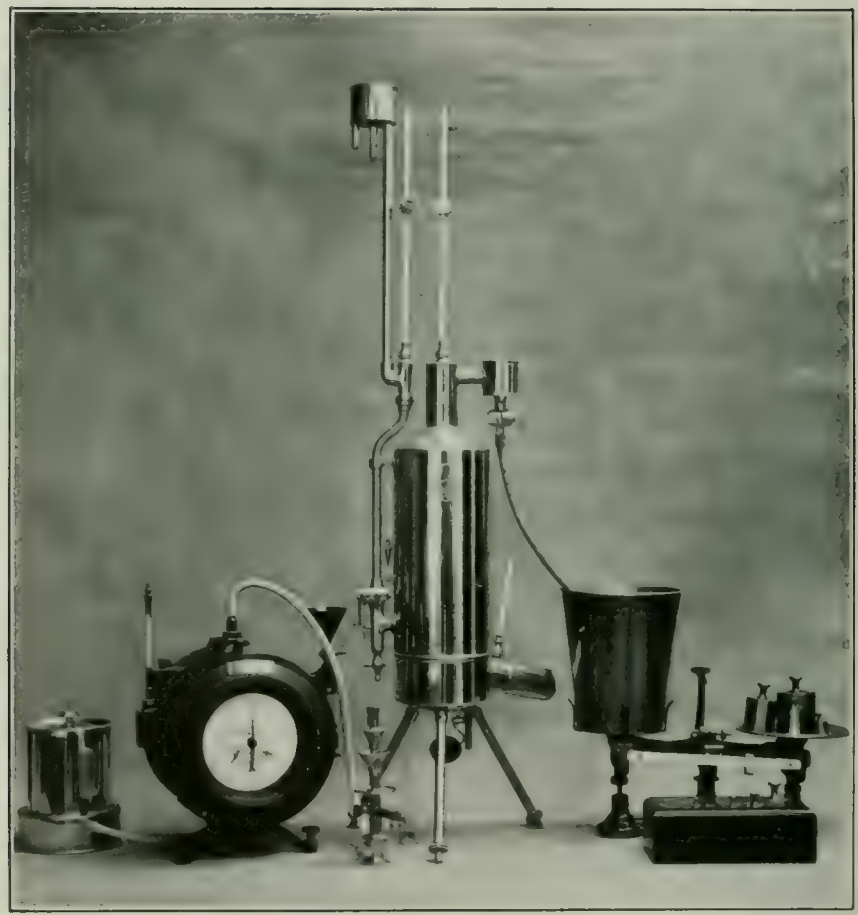


Fig. 22. *Hinman-Junkers calorimeter*

sidered on p. 50, where it was shown that the value of this ratio, for this calorimeter, was above 0.996.

Comparisons with Bomb Calorimeters.—The determinations of the total heating values of a sample of natural gas and of nearly pure hydrogen, the experimental data for which are given on p. 104 and p. 106, have shown that total heating values as determined with the Junkers calorimeter No. 1209, were in agreement with the heating values found with calorimeters of the Berthelot bomb type, to within the limits of experimental errors of the measurements (viz, about 0.3 per cent).

2. HINMAN-JUNKERS CALORIMETER

Description.—This calorimeter, illustrated in Fig. 22, is a close copy of the Junkers calorimeter described in the preceding section. Modifications have been made in a few minor details. The inlet and outlet water thermometers are mounted on the same level, both the inlet-water thermometer and the valve controlling the rate of water flow being in the descending stream of water. A three-way stopcock has been provided for diverting the effluent water to drain or to weighing bucket. In the later models the combustion chamber and the condenser tubes form a unit which can be removed from the casing to permit of cleaning the outside surfaces of the tubes which are in contact with the water, a feature which is very desirable, as it permits not only the removal of deposits from the outer surface of the condenser tubes, but also makes all parts of the calorimeter conveniently accessible for repairs. Each thermometer is mounted in a metal holder provided with a flange held in position by a screw cap, a mounting which makes the thermometers more liable to breakage than the flexible rubber stopper mounting used with other calorimeters, although, if the thermometer[21a] stems were protected by metal tubes with front and back suitably cut away to permit of reading and to provide for proper illumination, this type of mounting would be very serviceable in use. This calorimeter also differs from the Junkers calorimeter in the dimensions of some of the parts. The total water content is somewhat in excess of 3 pounds.

[21a] This form of mounting for the thermometers has been adopted in later models.

A calorimeter of this type (No. 91) was kindly placed at the disposal of the Bureau by Mr. J. B. Klumpp.

Special Tests.—It was found that reheating of the products at the base of the calorimeter could be prevented if the burner were raised as described in the preceding section relating to the Junkers calorimeter. The use of radiation shields on the burner, either those furnished with the instrument or others made of thin disks of aluminum suitably perforated, resulted in increasing the observed heating values by about 0.7 per cent. Later experiments with another calorimeter of the same type indicated that this increase was somewhat less than 0.5 per cent.

The size of the combustion chamber and of the spaces provided for the passage of the products of combustion are approximately the same as in the Junkers calorimeter. The damper furnished with the calorimeter had two one-half inch openings, and with this damper closed the normal rate of gas consumption was about 5 cubic feet per hour for illuminating gas (650 Btu) and about 3 cubic feet per hour for natural gas (1000 Btu).

One of the calorimeters tested was defective in that only part of the water resulting from the condensation of aqueous vapor from the products of combustion was discharged through the spout provided for this purpose, while the remainder dripped from the lower edge of the wall of the combustion chamber.

The efficiency of the calorimeter as a heat absorber, determined from experiments with the electric heating coil, was found to be above 0.996.

Measurement of Total Heating Value.—Two Hinman-Junkers calorimeters (Nos. 91 and 164) were used to measure the total heating values of three samples of gas, two of illuminating gas and one of natural gas. The total heating values of these samples were determined as described on p. 110. The results of these determinations showed that if the observed heating values found with the Hinman-Junkers calorimeter were corrected for surface losses (which were practically the same as for the original type Junkers calorimeter), for effect of atmospheric humidity (by Tables 19 and 20), etc., the total heating values thus found were in agreement (0.2 per cent) to within the limits of experimental error with the total heating values that had been found for the gases used in the tests.

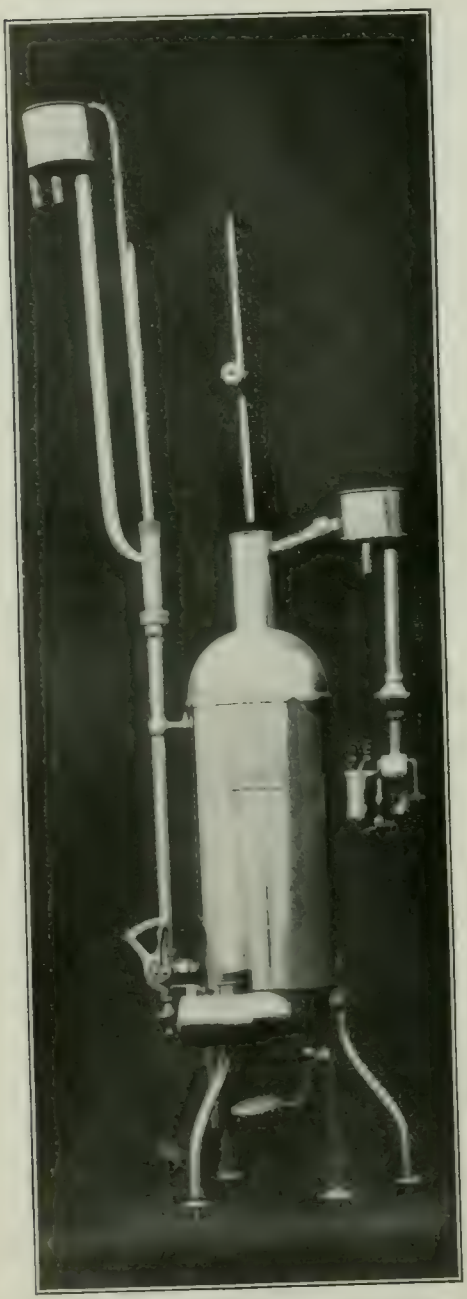


Fig. 23.—*Sargent calorimeter*

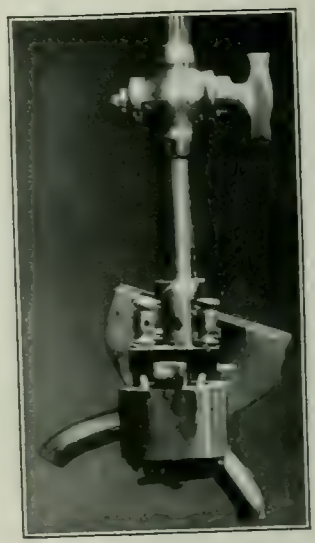


Fig. 23a.—*Enlarged view of automatic change-over device*

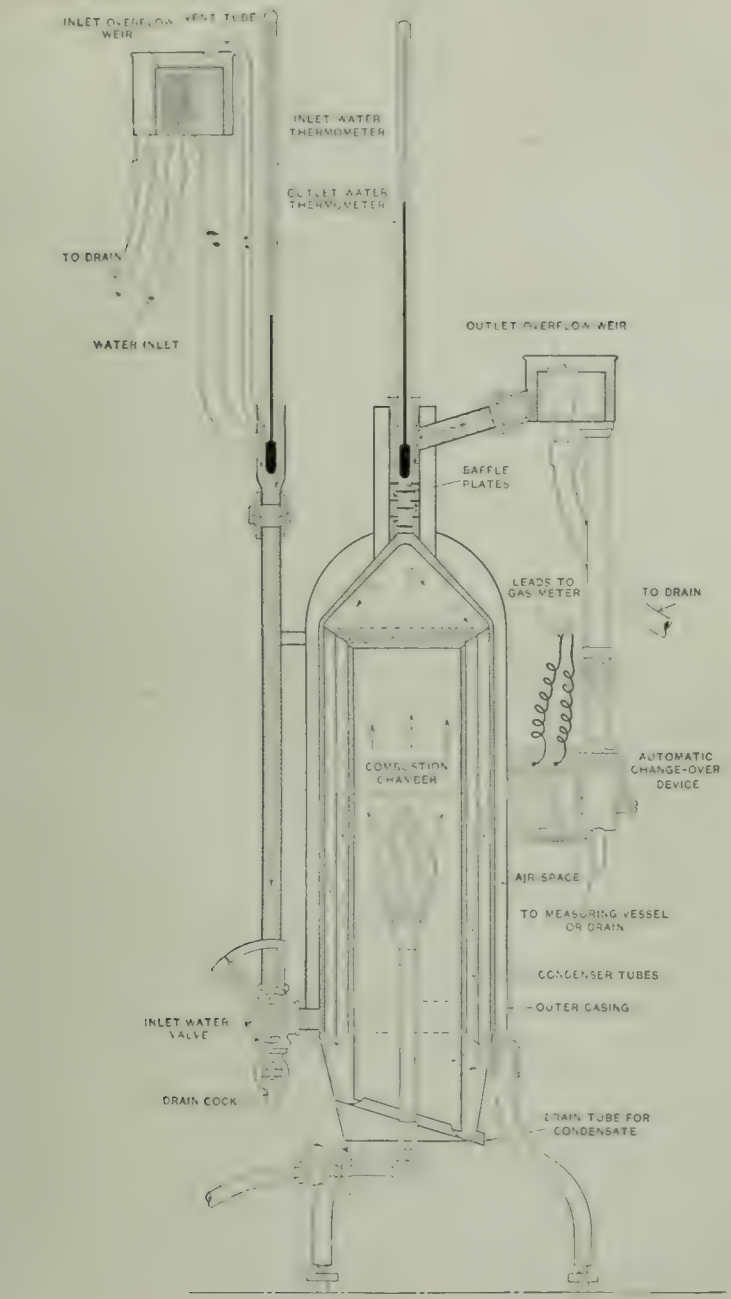


Fig. 24.—*Sargent calorimeter (section)*

3. SARGENT CALORIMETER

Description.—In the later models of this instrument the design of the Junkers calorimeter is followed very closely. In Figs. 23 and 24 are shown a photograph and a sectional drawing of one of these later models. A special feature is an automatic change-over device to divert the effluent stream of water from drain to weighing bucket, or vice versa. When the index of the meter passes through the zero position, it closes an electric circuit, thereby energizing an electromagnet which controls the operation of the change-over device. The inlet and outlet water thermometers are on the same level, and both the inlet-water thermometer and the valve controlling the rate of water flow are in the descending stream of water. A vent tube has been added for the purpose of permitting the escape of air which may accumulate around the bulb of the inlet-water thermometer. The total water content of this calorimeter is somewhat in excess of 3 pounds.

Special Tests.—The burner as furnished with the calorimeter could be set sufficiently high to avoid reheating of the combustion products in the products chamber at the base of the calorimeter, so that the products were discharged at practically the temperature of the inlet water. The radiation shields furnished with the burner, which were made of mica to permit observation of the flame in the calorimeter, gave the same result as perforated aluminum disk shields, the increase in the observed heating value due to the shields being of the order of 0.5 per cent.

The capacity of the spaces provided for the passage of the products of combustion is approximately the same as in the Junkers calorimeter. There were no openings in the dampers of the instruments tested. However, if the damper were made with two one-half inch openings, the normal rate of gas consumption, with damper closed, should be between 5 and 6 cubic feet per hour for illuminating gas. With the instrument as furnished, with no openings in the damper, the normal rate will depend upon the angular setting of the damper.

One of the calorimeters tested had to be modified to permit of the determination of net heating values, as part of the water

resulting from the condensation of aqueous vapor from the products of combustion collected in the outlet tube through which the products of combustion escaped.

The efficiency of one of the calorimeters as a heat absorber, determined from experiments with the electric heating coil, was found to be above 0.996.

Measurement of Total Heating Value.—Two Sargent calorimeters were used to measure the total heating values of several samples of illuminating gas. The total heating values of these samples were determined as described on p. 110. The results of these determinations showed that, if the observed heating values found with the Sargent calorimeters were corrected for surface losses (which were practically the same as for the original type Junkers calorimeter) for effect of atmospheric humidity (by Table 19), etc., the total heating values thus found were in agreement (0.2 per cent) to within the limits of experimental error with the total heating values that had been found for the gases used in the tests.

4. JUNKERS CALORIMETER (NEW TYPE)

Description.—This calorimeter, illustrated in Figs. 25 and 26, differs radically in design from the older type of Junkers calorimeter. The calorimeter is inclosed at the sides and top in a casing of thin sheet metal, nickel plated on the outside, the air space between the calorimeter proper and the outer casing being wide enough to accommodate the flattened tube through which the water from the inlet wier, after passing the bulb of the inlet-water thermometer at the top of the calorimeter, is led to the bottom of the calorimeter. The water then passes upward in an annular cylindrical shell, the inner wall of which forms the combustion chamber, outward at the top of this shell through four radial passages into the space above the combustion chamber, thence through a tube, in which is found the bulb of the outlet-water thermometer, to an overflow wier, from which it passes through a bent tube, which may be rotated in such a way as to divert the effluent stream from drain to graduate (or weighing bucket), or vice versa.

Both the inlet-water thermometer and the valve controlling the rate of water flow are in the descending stream of water. A

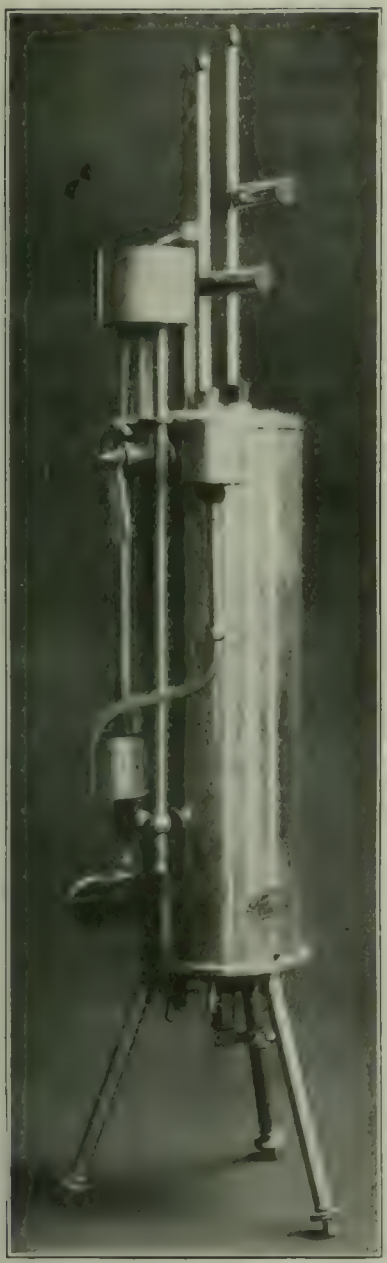


Fig. 25

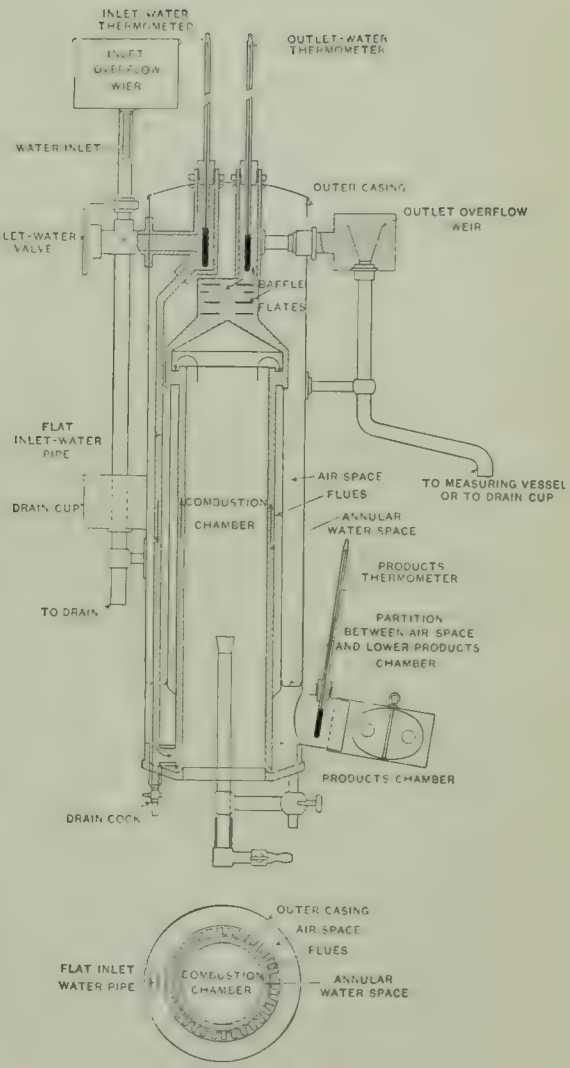


Fig. 26

Junkers calorimeter : new type

vent tube has been added for the purpose of permitting the escape of air that may accumulate around the bulb of the inlet-water thermometer. The total water content of this calorimeter is about 1.5 pounds. The inlet and outlet water thermometers are mounted on the same level. For this and for other reasons calorimeters of the new type are somewhat more convenient of manipulation than those of the older type.

The heated products of combustion pass upward to the top of the combustion chamber, thence downward through the spaces shown in Fig. 26 (which are formed by bending sheet metal to the shape shown in the illustration) and thence into the products chamber at the bottom of the calorimeter, from which the products are discharged through the outlet-products tube.

The calorimeter tested, No. 1443, was kindly loaned for the purpose of this investigation by Mr. J. C. Dickerman, at that time chief gas tester of the city of Chicago.

Special Tests.—In this calorimeter the lower products chamber is separated from the combustion chamber by the annular shell of water, so that reheating of the products is avoided if the burner is set well within the combustion chamber. Owing to the fact that the spaces in which the products pass downward are not completely surrounded by the upward stream of water, the products of combustion escape at a temperature slightly (about 1° F) above that of the inlet water.

The effect on the observed heating values of the use of radiation shields was not determined for this calorimeter, as the order of magnitude of the effect of such shields was known from experiments with other calorimeters.

The flue capacity of this calorimeter is somewhat less than that of the older type of Junkers calorimeter. The normal rate of gas consumption for illuminating gas was about 5 cubic feet per hour with the damper (two 15-mm openings) closed, and about 7 cubic feet per hour with the damper open.

The calorimeter is so designed and constructed that the drainage of the water resulting from the condensation of aqueous vapor from the products of combustion is uniform, so that net heating values can be accurately determined.

Error in Indications of Outlet-Water Thermometer.—Early in the tests the fact developed that displacing the bulb of the outlet-water thermometer sidewise a short distance in the outlet water tube caused changes in the indications of the thermometer of as much as 0.3° F, corresponding, for an 18° rise in temperature, to about 1.7 per cent in heating value. Mr. Dickerman suggested that a mixing device be mounted in the outlet water tube ahead of the thermometer bulb. A mixing device, of the form shown in Fig. 27, was accordingly constructed and mounted in the outlet tube of the calorimeter. This mixer caused the water to flow through a central tube, in which were mounted a number of conical diaphragms, which changed the direction of flow as indicated by the arrows. After passing the thermometer bulb the water passed out of the top of this central tube and flowed downward in the annular space between this tube and the outlet tube and out through the side tube leading to the overflow wier.

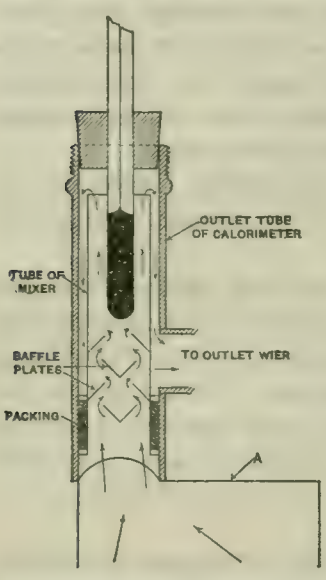


Fig. 27.—*Mixing device for outlet water in Junkers calorimeter (new type).*

With this mixer in position the thermometer apparently indicated the true mean temperature of the outlet water. It was found, however, that the readings of the outlet-water thermometer varied during the course of an experiment more than with the other calorimeters, probably on account of the accumulation of air bubbles under the nearly horizontal surface (A, Fig. 27), which caused a variation in the rate of flow of the water. That such was the case was indicated by the fact that shaking and tilting the calorimeter resulted in the visible liberation of air bubbles and in appreciable changes (over 1 per cent) in the rate of flow of water.

Determination of Total Heating Value.—The total heating value of a given sample of gas was determined as described on p. 110.

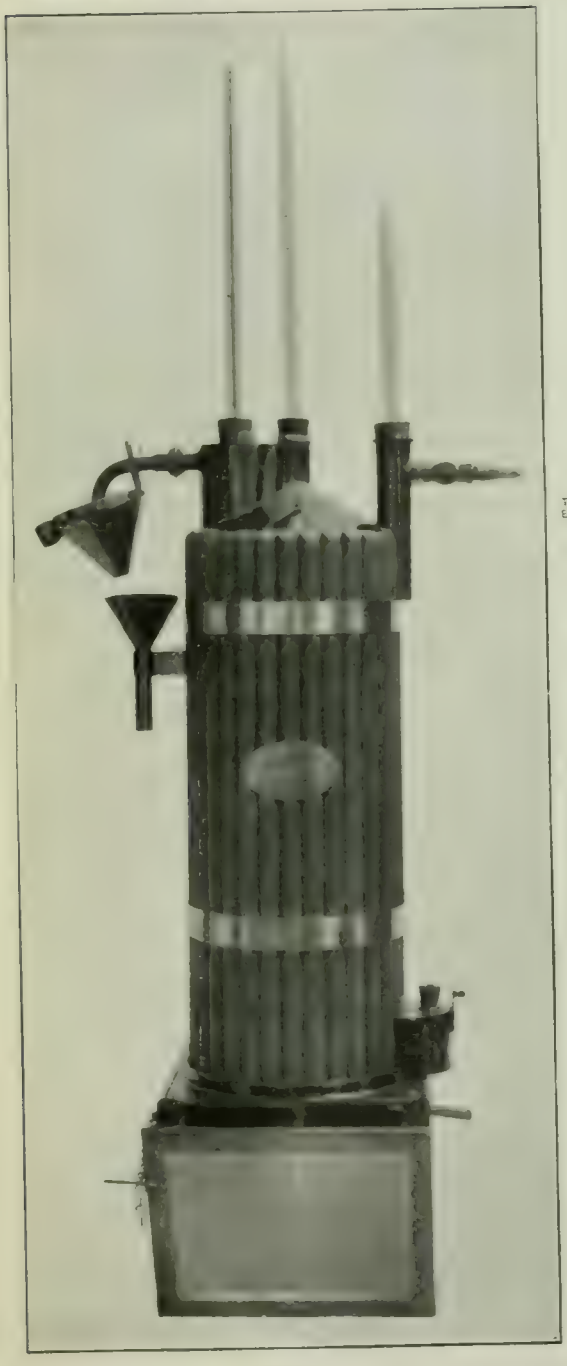


Fig. 28

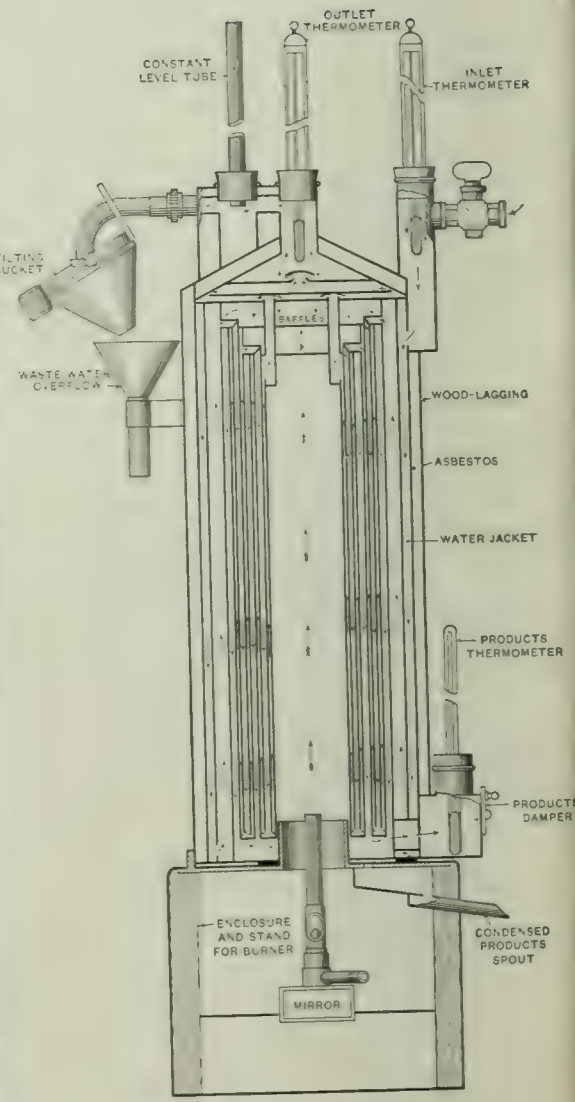


Fig. 29

Simmance-Abady calorimeter (English type)

Junkers calorimeter (new type) No. 1443, with the mixing device in the outlet-water tube and with radiation shields on the burner, was then used to measure the total heating value of the same gas. The results of a typical test are given in Table 28.

TABLE 28

Measurements of Total Heating Value with Junkers Calorimeter No. 1443 (New Type)

Calorimeter and method of operation	Total heating values
	Btu
Junkers No. 1209, operated at normal rate of 7 cubic feet per hour, damper closed	642
Junkers No. 1443, operated at normal rate of 5.1 cubic feet per hour, damper closed	641
Junkers No. 1443, operated at normal rate of 7.0 cubic feet per hour, damper open	641

The results show that, when the Junkers calorimeter No. 1443, new type, was provided with a suitable mixing device for the outlet water and with radiation shields on the burner, total heating values could be accurately determined.

5. SIMMANCE-ABADY CALORIMETER (ENGLISH TYPE)

Description.—This calorimeter, illustrated in Figs. 28 and 29, differs from the calorimeters already described in that the circulating water, instead of entering at the base of the calorimeter and passing upward and out at the top, enters a tube (in which is placed the bulb of the inlet-water thermometer) near the top of the calorimeter, passes downward in an annular space which is lagged on the outside with asbestos and wood and which forms the outer portion of the calorimeter, thence upward and downward in a series of concentric annular spaces, and finally out at the top of the calorimeter through a tube in which is placed the bulb of the outlet-water thermometer.

After passing the bulb of the outlet-water thermometer, the water enters a small space in which is supported a gauge glass and then is discharged from the calorimeter through a curved tube. A tilting bucket below this tube is provided to divert the water

from drain to graduate or vice versa. The total water content of calorimeters of this type is 12 to 14 pounds.

The inlet and outlet water thermometers are at the same level. No convenient means are provided for permitting the escape of air which may accumulate around the bulb of the inlet-water thermometer, so that it is desirable, before beginning a test, to loosen the stopper supporting this thermometer so as to permit the escape of the entrapped air.

The inner boundary of the last of the concentric annular spaces mentioned above forms the combustion chamber. The products of combustion pass upward to the top of the combustion chamber and thence downward, through one or the other of two annular spaces between the series of annular water spaces, to the base of the calorimeter, where they are discharged through an opening provided with an adjustable damper.

Special Tests.—The method of observation at one time recommended by the designers of this calorimeter, viz, single readings of inlet and outlet water thermometers and the measurement of the water flowing through the calorimeter during a fractional part of a turn of the index of the meter, does not permit of accuracy in a heating value test, for several reasons, among which may be mentioned (*a*) the time error in manipulation of the change-over device becomes too large in proportion to the short time required for the meter index to travel over, at most, 0.2 of a turn and (*b*) the amount of gas delivered during a fraction of a revolution by the wet meters furnished with these calorimeters is not proportional to said fraction of a revolution.

As the tilting bucket furnished with the calorimeter is suitable only for this method of observation, it was removed and a change-over funnel substituted. The gage glass also is not necessary unless the method of observation just referred to is followed. To insure constancy of water flow, a water supply at constant pressure must be provided external to the calorimeter, either by an overflow wier or other regulating device. With the calorimeters tested, the gage glass could not be used with the calorimeter as furnished, as the water flowing from the curved outlet tube at ordinary rates of flow drew in air through the gage glass, causing irregularity in the water flow.

In the tests made the gage glass was omitted and the outlet tube was turned through an angle slightly in excess of 90°, to permit the escape of air which otherwise accumulated in the bend of the tube.

It will be seen from Fig. 29 that in the instrument as furnished by the makers the burner is set so that the base of the flame is only a short distance above the lower boundary of the combustion chamber. On pp. 58, 59, it was shown that raising the burner 3 inches above the position indicated in Fig. 29 increased the observed heating values by about 1 per cent, while adding the radiation shields resulted in a further increase of about 0.5 per cent. In a subsequent experiment with another calorimeter the total increase in the observed heating value, due to raising the burner and to adding radiation shields, was found to be about 1 per cent. The burner should therefore be set so that the base of the flame is at least 3 inches within the combustion chamber.

With the burner raised and radiation shields added, the temperature at which the products of combustion were discharged was 3° to 4° F above that of the inlet water. The products of combustion were found to be saturated with water vapor at a temperature very approximately the same as that at which they escaped through the outlet, thus indicating that these products had not been cooled to the temperature of the inlet water. The cooling of the products is not as effective as it is in the calorimeters of the condenser-tube type already described, but the loss of heat due to this cause is relatively unimportant.

The rate of heat interchange between the calorimeter and its surroundings, when water, the temperature of which differed from the room temperature, was run through the calorimeter, with no gas burning, was found to be 0.055 Btu per minute per 1° F difference between water temperature and room temperature, i. e., about twice as great as for an air-jacketed calorimeter. It was found that wetting the wood lagging caused no appreciable difference in the rate of heat interchange.

The so-called radiation loss from the surface, when the calorimeter is operated with the inlet water at room temperature, is probably quite small, as practically the entire calorimeter with the

exception of a small part at the top is jacketed with the inlet water.

The normal rate of gas consumption for illuminating gas (650 Btu) was found to be about 7.5 cubic feet per hour, when the damper was open. The calorimeter is so constructed that only a portion of the products of combustion escape through the opening provided for that purpose, the remainder escaping through the space between the iron base-plate and the body of the calorimeter. As this opening was more or less obstructed by the asbestos and wooden lagging, the normal rate might have been different if the lagging had been slightly displaced.

The calorimeter is so designed and constructed that the drainage of the water formed by the condensation of aqueous vapor from the products of combustion is fairly regular, although improvement in this respect is desirable if net heating values are to be calculated from the amount of condensate delivered during the time that a small quantity of gas (about 1 cubic foot) is burned in the calorimeter.

The bulb of the outlet-water thermometer is surrounded by a perforated metal cone, apex downward. With this device in position the thermometer did not indicate the true mean temperature of the effluent water, as was shown in the experiments cited on p. 51. Accordingly a mixing device consisting of several baffle plates was substituted for the perforated cone. A mixing device similar to that made for the new type Junkers calorimeter would have been preferable, although the baffle-plate mixer proved satisfactory. With this mixer in position the efficiency of the calorimeter as a heat absorber, as determined from experiments with the electric heating coil, was found to be over 0.996.

The lag of the calorimeter is greater than that of the Junkers, Hinman and Sargent calorimeters, but is considerably less than that of the Boys calorimeter, as was shown on p. 83. On account of the large water content of this calorimeter (14 pounds), it is some three minutes after a change of temperature of the inlet water takes place before such change makes itself evident at the outlet-water thermometer, when the calorimeter is operated at normal rate of gas consumption for illuminating gas and with a rate of water flow such as to give 18° F rise in temperature of the outlet water.

On account of the large water content and also on account of the insulating material on the outside, which is in good thermal communication with the water flowing through the calorimeter, changes in the temperature of the inlet water will introduce greater errors into the results than in the case of the other calorimeters considered in this report. For the satisfactory use of this calorimeter a supply of water at constant temperature and sufficient for at least 30 minutes' operation, should be available.

Measurement of Total Heating Value.—A Simmance-Abady (English type) calorimeter (No. 1631) was used to measure the total heating value of a sample of illuminating gas. The total heating value of this sample was determined as described on p. 110. The Simmance-Abady calorimeter was operated under the following conditions: With inlet water at constant temperature, with normal rate of gas consumption (7.5 cubic feet per hour), with burner provided with radiation shields and raised 3 inches above the position indicated in Fig. 29, and with a baffle-plate mixer in the outlet-water tube. The result of this determination showed that, if the observed heating value found with the Simmance-Abady calorimeter were corrected for the effect of atmospheric humidity (by Table 19), etc., the total heating values thus found were in agreement (0.2 per cent), to well within the limits of experimental error, with the total heating value that had been found for the gas used in the tests.

NOTE.—Most of the criticisms that have been made relate to minor defects that are quite easily corrected by simple modifications in construction, e. g., the burner may be raised, a mixing device for the outlet water provided, the tilting bucket removed, etc. It will be seen that when these changes were made and when a water supply at constant temperature was used accurate results were obtained with this calorimeter.

6. BOYS CALORIMETER [22]

This calorimeter is illustrated in Figs. 30 and 31. The water enters at the top of the calorimeter, flows downward past the bulb of the inlet-water thermometer, then through five turns of copper pipe, having a helix of copper wire would on and sweated to the

[22] C. V. Boys, Proc. Roy. Soc., London, A-77, p. 122: 1906.

surface, after the manner of some motor-car radiators, to facilitate heat interchange between the combustion products on the outside and the water within the tube, then upward through four turns of similar radiator tubing, within and concentric with the first, and separated therefrom by an insulating brattice, Q. The water then passes through several turns of copper pipe wound on and sweated to the outer cylindrical surface of a bell-shaped brass casting forming the upper part of the combustion chamber, thence into a brass box which forms the upper part of the aforesaid casting and in which is a temperature-equalizing device consisting of two dished plates of thin brass, K K, held in place by three scrolls of thin brass, L L L, thence into the outlet tube, in which is found the bulb of the outlet-water thermometer, and thence is discharged from the calorimeter. The parts described are supported from a wooden top, G. Surrounding the outer turns of the radiator coil is a cylindrical mantle of thin sheet metal, which is also supported from the wooden top and which serves to protect the radiator coils and to support the calorimeter when the latter is removed from the outer casing, D. The total capacity of the water circulation system is small, the water content being only about 0.7 pound (300 cc).

The annular space between the outer casing, D, and the metal chimney, E, is closed at the bottom and is filled to a depth of about 1 inch with water (about a pound), in which the lower turns of the radiator coils are immersed. The level of the upper surface of this water is fixed by the position of the small drain tube, F, and the water condensed from the products of combustion is drained off through this tube.

The calorimeter rests on three metal supports, C, at a small distance above the metal plate which covers the wooden base, A, in which the double union jet (luminous flame) burner, B, is mounted.

The products of combustion pass upward through the metal chimney, E, impinge against the brass box, H, through which water is circulated and which forms the top of the combustion chamber, thence downward past the inner turns of the radiator coils, upward on the outside of the brattice, Q, past the outer turns of the radiator coils and out of the calorimeter through a number of holes in the wooden top, G. There is also an opening in this top

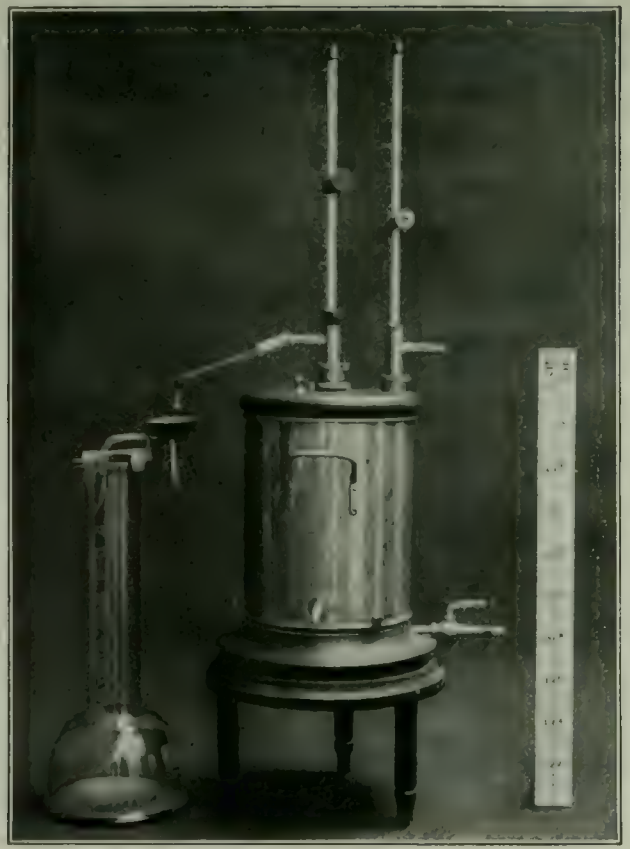


Fig. 30

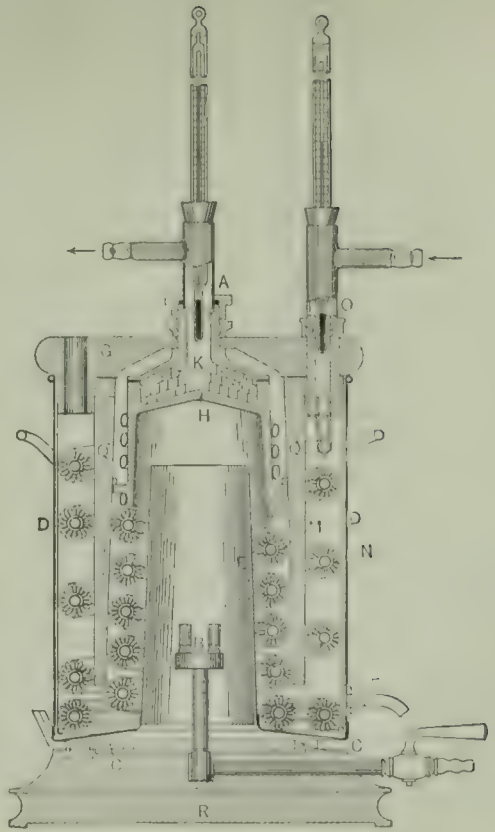


Fig. 31

Boys calorimeter (John J. Griffin & Sons)

for the thermometer intended for measuring the temperature of the outlet products. The various parts of the water circulation system are connected by union joints, so that the sections can be readily taken apart. To prevent corrosion, the calorimeter, when not in use, is lifted from its base and set into a jar containing a solution of sodium carbonate.

One of the features which the designer particularly emphasizes is that the water flows through the calorimeter in series, thus avoiding the fluctuations in the readings of the outlet-water thermometer due to insufficient mixing of unequally heated parallel streams of water.

Special Tests.—When the luminous flame burner was used and the rate of gas consumption was 4.7 cubic feet per hour, incomplete combustion set in, as was made evident by the appearance of black smoke in the products of combustion. This proved to be a very sensitive test of the occurrence of incomplete combustion, as very evident traces of smoke could be seen before the observed heating value had been diminished by 0.5 per cent. The normal rate of gas consumption for this calorimeter and for the illuminating gas tested (650 Btu) was about 3.3 cubic feet per hour.

The products thermometer, as it is mounted in this calorimeter in a small hole closed with a cork, can hardly be expected to give a reliable indication of the temperature of the products, as there is but little circulation of the products past the bulb. If the thermometer is inserted so that the bulb is below the bottom of the wooden cover it is brought into contact with the radiator coils. When mounted in a cork in the hole provided for this purpose, the products thermometer indicated a temperature about 5° to 6° F above that of the inlet water, while the actual temperature of the products, as indicated by a thermometer mounted with its bulb in one of the larger outlet product holes, so that the products flowed past the bulb, was only about 3° F above that of the inlet water.

The gain or loss of heat due to a difference of 1° C (1°8 F) between the temperatures of the surrounding air and of the escaping products of combustion, is very small, apparently much smaller than is indicated in the rule given by Boys, viz, "The correction

for rise or fall of temperature of the air passing through the instrument is as near as possible one-third (or one-sixth in later publications) of a calorie to the cubic foot of gas for each 1° C of change." The assumption made in the deduction of this rule was that the ratio of volumes air to gas was about 8¼ to 1. A simple computation [23] shows that under the above conditions the gain or loss of sensible heat is more nearly one-sixteenth Calorie instead of one-third (or one-sixth) Calorie to the cubic foot of gas for each 1° C of change. If the gain or loss of heat due to the difference in the amounts of water vapor carried into and out of the calorimeter is considered, the correction depends not only upon the volumes and the temperatures but also upon the degrees of saturation of the entering air (and gas) and of the escaping products, and is not proportional merely to the difference in the temperatures of air and products.

The time required for this calorimeter to attain thermal equilibrium after lighting the gas or after any change in the rate of heat supply to the calorimeter has taken place (e. g., due to a change in the heating value of the gas) is somewhat less than for the Simmance-Abady (American type) calorimeter, which is of very similar construction, but is greater than for any of the other flow calorimeters included in this investigation. It was pointed out on p. 83 that a small water content does not necessarily mean that the lag will be small. The large lag of this calorimeter is due to the presence of considerable amounts of poorly conducting material that enter into the construction of the calorimeter, the presence of a considerable mass of still water in the bottom of the calorimeter, and the use of a heavy metal chimney and a heavy brass casting to form the combustion chamber.

The advantage claimed for this calorimeter, that the water flows in series through the calorimeter and that the difficulties arising from insufficient mixing of parallel unequally heated streams of

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[23] Eight and one-fourth cubic feet of air per cubic foot of gas burned correspond to about 7.8 cubic feet of products per cubic foot of gas burned. The weight of 1 liter of products is about 1.2 grams, and the specific heat is approximately 0.23. Therefore, if the products are 1° C warmer than the entering air, they will carry out an amount of sensible heat given by

$$7.8 \times 28.3 \times 1.2 \times 0.23 = 61 \text{ small calories}$$

$$= \frac{1000}{61} = \frac{1}{16} \text{ large calorie.}$$

In the above computation a number of minor factors have been neglected. A complete analysis of all the heat interchanges involved is given in previous sections of this report.

water are thus obviated, might be expected from theoretical considerations, yet the fact remains that the application of the principle, on account of the presence of certain sources of error in the two calorimeters in which it has been applied, has not resulted in a calorimeter of as high accuracy as the parallel flow calorimeters. The readings of the outlet-water thermometer, it is true, are not subject to as large fluctuations as are the readings of the outlet-water thermometers of the other calorimeters, but this is undoubtedly in part due to the large lag of this calorimeter, which is less sensitive to sudden variations in the rate of heat supply.

The drainage of the water formed by the condensation of aqueous vapor from the products of combustion was frequently very irregular, as is to be expected where the drainage takes place from the top of a water surface of large area, even when precautions were taken to prevent contact between the outer casing and the metal shield around the radiator coils.

The experiments on the efficiency of this calorimeter as a heat absorber, as determined with an electric heating coil mounted in the combustion chamber, did not lead to satisfactory results as was explained on p. 51, but served to indicate that the efficiency was lower than for the other calorimeters on account of the favorable conditions for conduction of heat to the base and other parts of the calorimeter. This conclusion was corroborated by the results of the experiments summarized below.

Determination of Total Heating Value.—The total heating value of a given sample of gas was determined as described on p. 110. The Boys calorimeter No. 67 was then used to measure the heating value of the same sample of gas. The data of such a test are given in Table 29. It will be seen from this table that the heating values found with the Boys calorimeter are about 2 per cent low. A similar series of tests made August 1, 1912, gave practically the same result (1.8 per cent).

The net heating values determined by the two calorimeters, if calculated from the data given in Table 29 and footnote c, would be in fairly good agreement, but this is due to the abnormally small volume of condensate delivered by the Boys calorimeter in this test. In the test of August 1, 1912, the volume of condensate delivered by the Boys calorimeter was about 1 cc per cubic foot

of gas greater than that delivered by the Junkers calorimeter, so that the net heating value found with the Boys calorimeter in that test was over 2 per cent low.

The heat losses from this calorimeter were appreciably reduced by the following changes: (*a*) The substitution of a porcelain stem Bunsen burner for the luminous flame burner furnished with the calorimeter; (*b*) the separation of the sheet-metal bottom from the wooden base on which it rests by interposing three small insulating blocks. The addition of radiation shields to the porcelain stem Bunsen burner caused no further certain diminution in heat loss. When the Bunsen burner was used the normal rate of gas consumption depended to a considerable extent upon the character of the flame—e. g., by making the flame strongly oxidizing the normal rate could be increased to 5 or 6 cubic feet per hour. When the Bunsen burner was adjusted to make the normal rate 3.5 cubic feet per hour, the heating values found with the calorimeter were still over 1 per cent low.

In an editorial notice in the London Journal of Gas Lighting for April 14, 1914, the question was raised as to whether the conclusion reached by the authors, viz, that the Boys calorimeter No. 67 gave heating values about 2 per cent low, was applicable to the Boys calorimeter as a type, or whether the instrument tested was defective. Since that date a further and most exhaustive series of tests has been made on the Boys calorimeter No. 67 and on another Boys calorimeter, No. 60, loaned by Mr. J. B. Klumpp. Alternate measurements were made with the Junkers calorimeter No. 1209 and with the Boys calorimeters on the same sample of gas drawn from a holder. The same meter was used, thus diminishing the errors of metering; furthermore, in some of the tests the same pair of thermometers was used in all the calorimeters. The results of a large series of such tests again gave the result that the observed heating values found with the Boys calorimeter No. 67 were 2 per cent lower than those found with the Junkers calorimeter, while the absorbed heating values found with the Boys calorimeter No. 60 were over 1 per cent lower.

The lower values found with the Boys calorimeter No. 67 were due in part at least to the fact that a relatively small part of its radiator coils was immersed in the still water in the bottom of the

calorimeter, with the result that this water became appreciably heated during the operation of the calorimeter. Calorimeter No. 67 had 9½ turns of radiator coil while No. 60 had 10 such turns.

TABLE 29

Comparison of Boys Calorimeter No. 67 with Junkers Calorimeter No. 1209 (Sept. 3, 1913)

Experiment No.	1	2	3	4	5	6
Calorimeter	Junkers No. 1209		Boys No. 67		Junkers No. 1209	
Time of beginning test	2–51	2–54	[a] 3–13	3–19	3–40	3–44
Room temperature	81°	81°	82°	82°	82°	82°
Atmospheric humidity	68%	.....	67%	.....	68%	.....
Products temperature	82°	82°	[b] 87°	[b] 87°	82°	82°
Condensate for 1 cu. ft. gas	19.6 cc		erratic [c]		19.8 cc	
Rate of gas consumption [d]	6.9	6.9	3.2	3.2	6.8	6.8
Temperature of inlet water, corrected	82°04	82.04	82°00	82.00	81°95	81.95
Temperature of outlet water, corrected	100°38	100°38	100°40	100.40	100°00	100°00
Temperature difference	18°34	18°34	18°40	18.40	18°05	18°05
Water collected, pounds	6.459	6.462	6.327	6.332	6.574	6.585
Volume of gas at 60° F, 30 ins	0.1900	0.1900	0.1899	0.1899	0.1898	0.1898
Observed heating value, Btu	623.4	623.8	613.0	613.5	625.2	626.2
Correction for radiation	+0.6	+0.6	(e)	(e)	+0.6	+0.6
Correction for sens. heat of products	.....	.....	+0.6	+0.6	.....	.....
Correction for (inlet minus room) temperature [f]	+0.4	+0.4	0.0	0.0	0.0	0.0
Correction for latent heat of condensate	−45.1	−45.1	.....	.....	−45.5	−45.5
Net heating value, Btu	579	580	.....	.....	580	581
Observed heating value, Btu	623.4	623.8	613.0	613.5	625.2	626.2
Correction for radiation	+0.6	+0.6	.....	.....	+0.6	+0.6
Correction for sens. heat of products	.....	.....	+0.6	+0.6	.....	.....
Correction for (inlet minus room) temperature [f]	+0.8	+0.8	0.0	0.0	0.0	0.0
Correction for atmospheric humidity [g]	+2	+2	+2	+2	+2	+2
Total heating value, Btu	627	627	616	616	628	629

[a] The Boys calorimeter had been in operation over an hour on a separate supply of gas, giving the same temperature rise, and was switched over to gas under test without extinguishing the flame.

[b] Reading of thermometer mounted in cork in hole in cover of calorimeter.

[c] Condensate collected was 16 cc. Evidently too little.

[d] The rate of gas consumption was the normal rate for each calorimeter.

[e] The several corrections for heat losses to surroundings were not determined separately for this calorimeter. The results of this and other tests show that these heat losses amount to about 11 or 12 Btu, i. e., nearly 2 per cent.

[f] Correction for difference between inlet water and room temperatures taken from Table 21.

[g] Correction for effect of atmospheric humidity taken from Table 19.

Further experiments with other Boys calorimeters are planned, and the results will probably be published in the Journal of Gas Lighting.

7. SIMMANCE-ABADY CALORIMETER (AMERICAN TYPE) [24]

Description.—The calorimeter is illustrated in Figs. 32 and 33. As will be seen from the illustration, features of the Boys and Simance-Abady (English type) calorimeters have been incorporated into this instrument. The water enters the tube, in which is placed the bulb of the inlet-water thermometer, at the top of the calorimeter, flows downward in an annular space and then upward in a spirally wound radiator coil, thence through several turns of copper pipe wound on and sweated to the outer cylindrical surface of a bell-shaped brass casting forming the upper part of the combustion chamber, thence into a brass box which forms the upper part of the aforesaid casting, and in which is a temperature equalizing device similar to that used in the Boys calorimeter, thence into the outlet tube in which is placed the bulb of the outlet-water thermometer. After passing the bulb of the outlet-water thermometer, the water is led to another upright tube in which is supported a gage glass, and then is discharged from the calorimeter through a curved tube into a tilting bucket. The gage glass, outlet tube, and tilting bucket are the same as are used in the English type Simmance-Abady calorimeter, and the discussion of these features in the section relating to that calorimeter is also applicable to this instrument. The annular water space is surrounded by a casing of thin sheet metal inclosing a narrow air space. The various connections in the calorimeter are made with union joints, so that it can be taken apart for cleaning or repairs.

The products of combustion pass upward in the combustion chamber, which is formed by a heavy metal tube, impinge against the water-cooled casting at the top, flow downward past the radiator coils in the space between the combustion chamber and the outer annular water space, and are discharged from the calorimeter through an opening provided with an adjustable damper.

Special Tests.—On page 58 it was shown that by using a longer burner stem, so that the base of the flame was about 4 inches above the lowest line of water circulation, the observed heating values were increased by over 1 per cent, and that the use of shields on the burner, in its raised position, resulted in a further increase of several tenths of 1 per cent. With the burner raised and shielded,

[24] The calorimeter tested was kindly loaned for this investigation by the Precision Instrument Co.

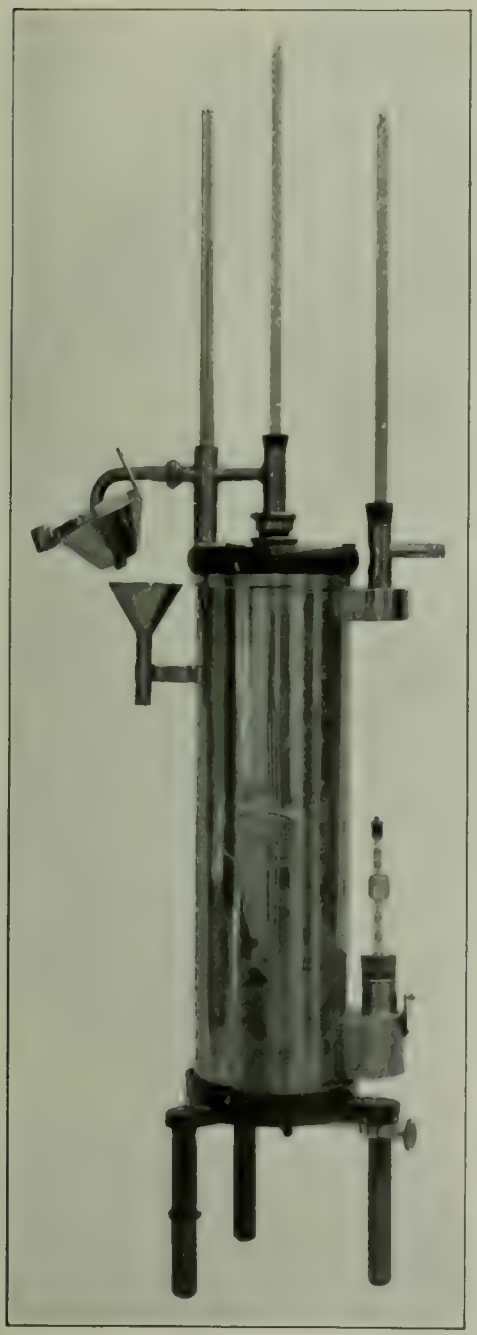

Fig. 32

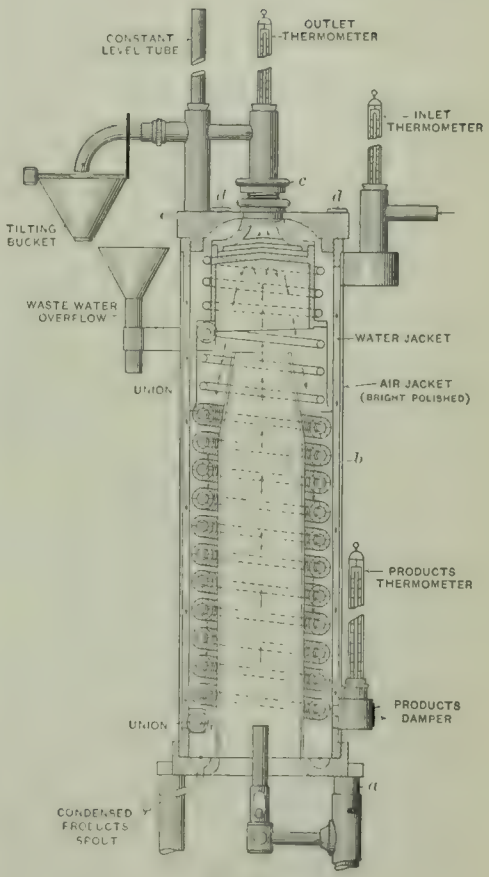

Fig. 33

Simmance-Abady calorimeter (American type)

the temperature at which the products of combustion were discharged was about 6° F above that of the inlet water when the combustion chamber consisted of the heavy metal tube with which the calorimeter was provided. When a light metal tube was substituted, the excess of temperature was reduced to 1.5° F. The rate of heat interchange between the calorimeter and its surroundings, when water, the temperature of which differed from that of the room, was run through the calorimeter, with no gas burning, was found to be about 0.05 Btu per minute per 1° F difference between water temperature and room temperature. The so-called radiation loss from the outer surface, when the calorimeter is operated with the inlet water at room temperature, is probably quite small, as nearly the entire calorimeter is jacketed with the inlet water.

The normal rate of gas consumption for illuminating gas (650 Btu) was found to be about 3.5 cubic feet per hour when the damper was open.

The calorimeter is so designed and constructed that the drainage from it, of the water formed by the condensation of aqueous vapor from the products of combustion, is fairly regular, so that the heat imparted to the calorimeter by the condensation of water vapor can be accurately determined. Net heating values can therefore be determined with this calorimeter as accurately as can total heating values (see below).

On page 86 it was shown that the lag of this calorimeter was greater than that of any of the other calorimeters tested, due in part to conduction of heat to the metal base of the calorimeter by the heavy metal tube forming part of the combustion chamber. When a light metal tube was substituted the lag was considerably reduced.

The efficiency of this calorimeter as a heat absorber, as measured with an electric heating coil in the combustion chamber, was about 0.99, the somewhat lower efficiency than that of other calorimeters being undoubtedly due, in part, to the conduction of heat to the metal base of the calorimeter through the heavy metal tube forming part of the combustion chamber.

Determinations of Heating Values.—Two calorimeters of this type were tested. The total heating value of a given sample of

gas was determined as described on page 110. The calorimeter under test, with burner raised and provided with radiation shields, was then used to determine the heating value of the same sample of gas. When the combustion chamber consisted of the heavy metal tube (2.6 pounds), the heating values found with this calorimeter were about 1 per cent low. When a light metal tube (0.27 pound) was substituted, the heating values found were less than 0.5 per cent low.

8. DOHERTY CALORIMETER [25]

Description.—The principle on which the action of this calorimeter is based may be briefly described as follows: The calorimeter proper is similar in principle to the other flow calorimeters, the heat generated by the combustion of the gas in a Bunsen burner being imparted to a stream of water flowing through the surrounding calorimeter. The water after leaving the calorimeter enters a tank which contains the sample of gas to be tested, and thereby displaces through the burner a volume of gas equal to the volume of water passed through the calorimeter, provided that the temperature of the gas remains uniform and constant throughout. The uncorrected heating value in Btu per cubic foot of gas, measured at the temperature and pressure existing in the gas tank, is found by multiplying the rise in temperature of the water by the number of pounds in a cubic foot of water at the outlet water temperature.[26] The heating value so obtained is then corrected to the standard conditions for measurement of gas (60° F, 30 inches) to find the observed heating value as defined on page 14. The volume of gas burned being equal to the volume of water heated, it is not necessary to measure these volumes independently; so that the use of the gas meter and the weighing of the water, necessary with the usual type of flow calorimeter, is dispensed with. A calorimeter operating on this principle would seem to be adapted for use as a recording calorimeter, as it automatically maintains a constant ratio of volume of gas to volume of water; so that only changes in the heating value or in the tem-

[25] The calorimeter No. 16 was kindly loaned for this investigation by the Improved Equipment Co.

[26] Inasmuch as the water is measured volumetrically, the heat capacity of a cubic foot of water for various outlet-water temperatures may be found, without sensible error, by multiplying the weight of a cubic foot of water at 60° F, viz, 62.4 pounds, by the appropriate factor taken from Table 22, p. 91.

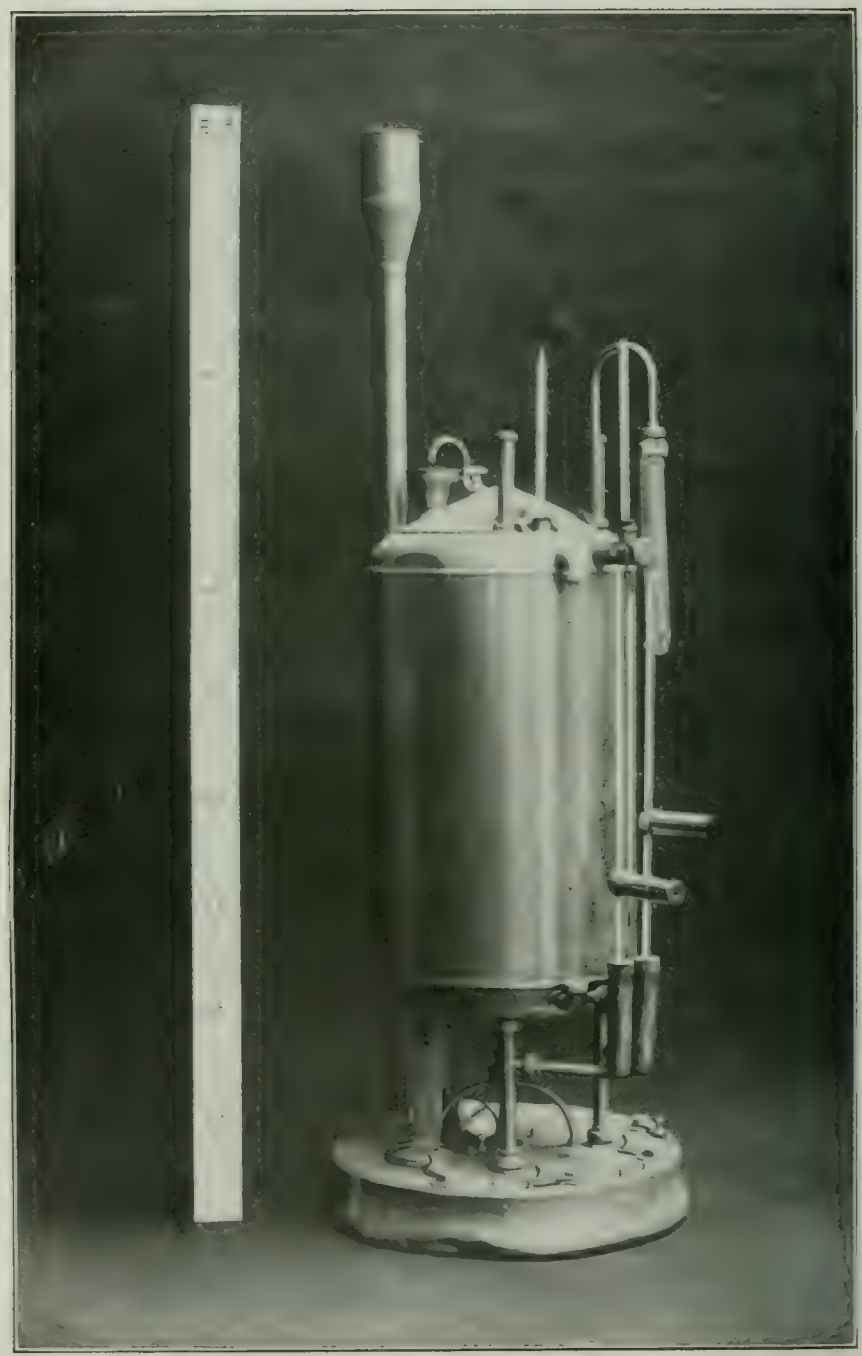

Fig. 34. *Doherty calorimeter*

perature or in the pressure of the gas produce changes in the temperature rise of the water flowing through the calorimeter. Arrangements would have to be made for automatically refilling the tank with gas, and if only one tank were used the record would be discontinuous. In a recording instrument the two thermometers would of course be replaced by a differential mechanical or electrical thermometric device combined with a suitable recorder.

The calorimeter is shown in Fig. 34. The internal connections are too complicated to be shown clearly in a single sectional drawing. For details of construction the reader is referred to the patent specifications, United States Letters Patent No. 828306. The essential principles of construction are shown in the diagrammatic sketch, Fig. 35. The water flows through the calorimeter under a pressure determined by the difference in level between the inlet wier A and the outlet wier B. The rate of flow is regulated by a throttle valve C beyond the outlet of the calorimeter. The water, passing the inlet-water thermometer I, enters the bottom of the calorimeter and flows upward in two concentric annular spaces D E, through a mixing chamber F, at the top, and down through a pipe G, between the two annular spaces, past the outlet-water thermometer O, and thence to the outlet wier B. From the outlet wier the water is discharged through a pipe H into the bottom of the gas tank K, and displaces the contained gas through the circuit leading to the Bunsen burner. The pressure of the gas in the tank is controlled by manipulating the two valves C and L, and is equal to atmospheric pressure plus the pressure shown by the manometer M. The level of the water in the gas tank is shown on the graduated gauge glass N. After all the gas is expelled from the tank and the latter is full of water the water from the calorimeter continues to discharge from the outlet wier by another passage, P, into the drain. The outlet wier is placed so that the water in the tank will not rise above the level Q and flood the gas pipes R S, leading to and from the gas tank. In the instrument, as actually constructed, the annular gas tank surrounds the calorimeter.

The Bunsen burner is placed within the inner of the two concentric annular water channels D E. The products of combustion

pass upward through the central combustion chamber T, through one of a number of openings in the top of this chamber, depending upon the position of an adjustable damper U, past a series of baffle plates in the space between the concentric water channels D and E, and are finally discharged into the air through a vent V, at the

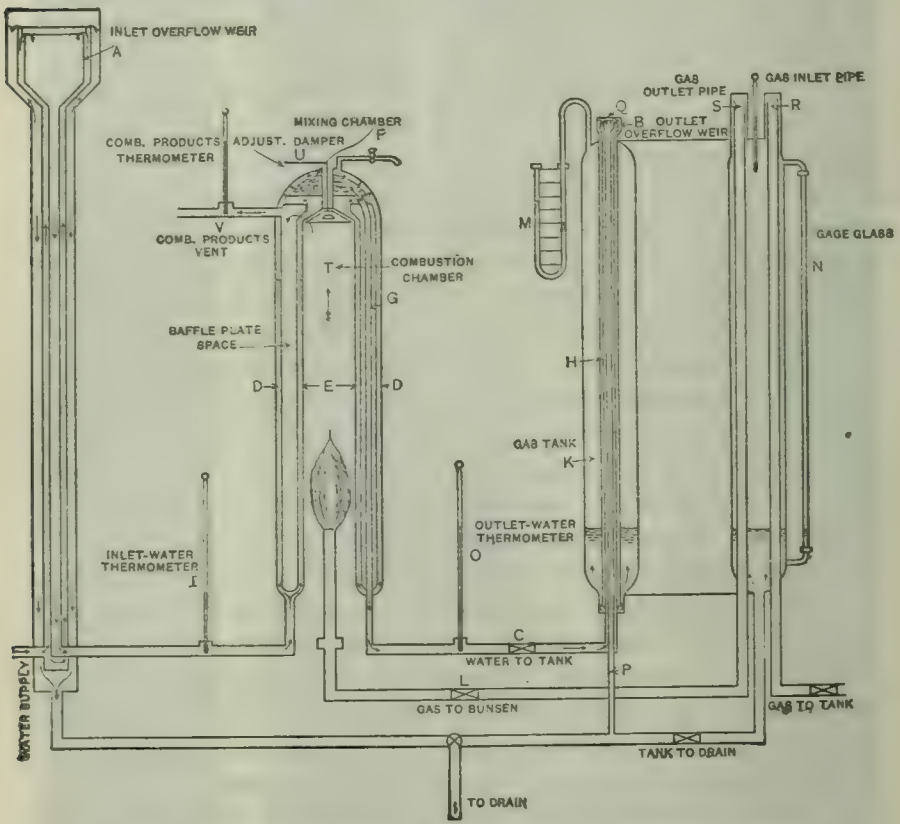

Fig. 35.—*Diagrammatic sketch illustrating construction and principle of operation of Doherty calorimeter*

top of the calorimeter, where their temperature is taken with a thermometer. The position of the damper determines the length of the path in the baffle plate space that the products of combustion must traverse, and therefore the temperature, within certain limits, at which they are discharged from the calorimeter.

On account of the complexity of connections and inacessibility of parts repairs to this calorimeter would be verv difficult to make.

Special Tests.—The first tests made consisted in a determination of the efficiency of the calorimetric part of the apparatus as a heat absorber when operated under various conditions. For this purpose the piping was disconnected just beyond the outlet-water thermometer and a rubber tube connection used to carry the water discharged from the calorimeter to a change-over funnel, thus permitting weighing of the water as with the usual flow calorimeters. The gas was supplied through a gas meter of the usual type. The calorimeter was operated at various rates of gas consumption from 1.7 to 3.7 cubic feet per hour, the damper being set to give the minimum temperature obtainable for the combustion products.

Combustion ceased to be complete at a rate of gas consumption of about 3.7 cubic feet per hour, and therefore the normal rate of gas consumption for the gas tested and for the damper setting used was about 2.6 cubic feet per hour. If the damper had been set differently, the normal rate might not have been the same, the difference depending upon the relative resistance to the flow of the combustion products around the baffle plates and through other parts of the flue spaces.

Alternate experiments were made on the same sample of gas using the burner with and without radiation shields. It was found as the result of these experiments that the loss of heat through the open bottom of the calorimeter (i. e., without shields) was less than 0.5 per cent. In view of the inconvenience in the use of shields with this calorimeter and of the presence of other errors, discussed subsequently, it was decided to omit the shields in subsequent experiments.

The calorimeter gave heating values about 1.3 per cent low, when operated as a flow calorimeter of the usual type, i. e., in connection with a gas meter, and under the following conditions: Inlet water at room temperature, surrounding gas tank empty and at room temperature, burner without shields, damper set to give maximum cooling of products of combustion, and gas burned at

normal rate. It will be shown subsequently that, with the proper method of operating the Doherty calorimeter, the lower calorimetric efficiency of the instrument tested (No. 16) was largely compensated by the gain of heat from the surrounding gas tank. The lower calorimetric efficiency is accounted for by (*a*) the high temperature of the exhaust products, (*b*) heat losses through the open bottom, and (*c*) heat losses to the surroundings, which are of relatively more consequence for this calorimeter than for calorimeters in which the rate of supply of heat is greater.

The combustion-products thermometer indicated that the temperature of the products was about that of the outlet water, but the true temperature was considerably higher, as was shown by removing the combustion-products tube and inserting a small thermometer some distance back into the horizontal space through which the products escaped. It was found that the products of combustion, when the damper was set for maximum cooling, escaped from the calorimeter saturated at a temperature about 1° F above that of the inlet water, indicating that they had been cooled down nearly to the temperature of the inlet water and then reheated before escaping at the top of the calorimeter.

This calorimeter will give somewhat different results depending upon its method of operation, due principally to the fact that the true rate at which the gas is being displaced from the gas tank will, in general, differ from the apparent rate as determined by the volume of the displacing water and from the temperature indications of the thermometer mounted in the top of the gas tank, unless the conditions of operation are such that the temperature of the gas is uniform and constant throughout.

Three methods of operation representing conditions likely to be encountered in practice were used. These were:

(*a*) With the temperature of the inlet water about 10° F below that of the room, and the outlet water therefore at room temperature, the tank having been filled with gas by displacing from it water at room temperature.

(*b*) With the temperature of the inlet water about equal to that of the room, and the outlet water which displaced the gas therefore about 10° F above room temperature, the tank having been filled with gas by displacing from it water at room temperature,

so that the tank and the contained gas were initially at room temperature.

(*c*) With the temperature of the inlet water about equal to that of the room, but the tank having been filled with gas by displacing from it water about 10° F warmer than the room temperature (outlet water), so that the tank and the contained gas were initially at a temperature above that of the room.

Method (*a*) is the ideal method of operation, in that it avoids uncertainties in the true mean temperature of the gas, the gas being initially at room temperature, and being displaced by water at room temperature, so that the errors in the measurement of the gas are minimized, and therefore observations made at various times during the progress of an experiment all lead to the same calculated heating value, which is not the case with method (*b*) (see below).

In the preliminary experiments it was found that this calorimeter when used as an ordinary flow calorimeter, gave results about 1.3 per cent low. It was also found, by running water through the calorimeter with no gas burning, but with the outer gas tank filled with water at room temperature, the inlet water being about 10° F colder, that the water was heated in its passage through the calorimeter, the outlet-water thermometer indicating a rise of temperature of 0.12° F at the rate of water flow used in the experiments. This rise of temperature was due to the heat conducted from the gas tank, through the felt insulation, to the inclosed calorimeter. In a heating-value test the amount of heat thus communicated will be somewhat less than under the conditions of the above experiment. It is evident that when the calorimeter is operated by method (*a*), the gain of heat due to operating the calorimeter with inlet water below room temperature and the resulting conduction of heat from the gas tank will tend to compensate for the effect of the lower calorimetric efficiency. It is shown in Table 30 that the compensation for the instrument tested was very close.

In method (*b*) the rate at which the gas is being displaced from the gas tank can not be correctly determined by the volume of the displacing water and from the indications of the thermometer in the gas tank. The gage glass on the front of the calorimeter

shows the level of the water in the gas tank. The lowest graduation of this glass is so placed that about one-fourth of the volume of gas in the tank is burned before the meniscus showing the water level reaches this graduation, during which interval the calorimeter is coming to an equilibrium condition. Inlet and outlet water thermometer readings, made at frequent intervals while the meniscus was moving over the entire graduated scale of the gage glass, were divided into three groups, corresponding to the first, middle, and last three graduation intervals. When these three groups of readings were used separately to calculate the heating value, on the assumption that the reading of the thermometer in the top of the gas tank gave the temperature of the gas, it was found that the first group gave a value 0.6 per cent higher than the middle group and 1 per cent higher than the last group of observations. The mean heating value, calculated from readings taken while the meniscus traversed the entire graduated part of the gauge glass, was about 0.8 per cent lower than the heating value found when the calorimeter was operated by method (*a*), as is shown in Table 30.

In method (*c*) the inlet water was at room temperature, but the gas tank, initially filled with water about 10° F above room temperature (outlet water temperature), was filled with gas as rapidly as possible by displacing the warm water, and the calorimetric experiment was begun immediately. Under these conditions of operation, as may be seen from Table 30, the heating value found was about 1.2 per cent lower than when the calorimeter was operated by method (*a*). As in method (*a*), the heating values calculated from observations made while the meniscus was at different positions in the gage glass did not differ appreciably. If the calorimetric experiment had not been started until some time after the tank had been filled with gas, the tank and contained gas would have attained the room temperature, and method (*c*) would have become identical with method (*b*).

The Doherty calorimeter is not so well adapted to the accurate determination of net heating values as is a flow calorimeter of the usual type.

Total Heating Value.—The method by which observed heating values, found with the usual type of flow calorimeter, may be cor-

rected to total heating values has been considered in previous sections of this report. The reduction of observed heating values obtained with the Doherty calorimeter to total heating values involves so large a number of separate factors that it would require an elaborate series of experiments to determine the magnitude of each of the factors separately. It can readily be shown that if the observed heating values obtained with the Doherty calorimeter are in agreement with those obtained with a flow calorimeter of the ordinary type, at a given atmospheric temperature and humidity, they will also be in agreement at all other humidities and at all temperatures ordinarily prevailing in the laboratory. It may be seen from Table 30 that when the Doherty calorimeter No. 16 was operated according to method (*a*), described above, the observed heating values found were in agreement with those found with Junkers calorimeter No. 1209. If this result is true in general for this type of calorimeter, the corrections for effect of atmospheric humidity, given in Tables 19 and 20, may be applied to the observed heating values found with the Doherty calorimeter, although the basis for this procedure is purely empirical. For example, for the tests summarized in Table 30 the average room temperature and humidity were 80° F and 40 per cent, respectively. The corresponding correction from Table 19 is +5 Btu, and hence the total heating value =660+5=665 Btu.

TABLE 30

Comparison of Doherty Calorimeter No. 16 with Junkers Calorimeter No. 1209

Calorimeter	Method of operation	Observed heating value
		Btu
Junkers	Operated at normal rate, with radiation shields on burner, inlet water at room temperature.	660
Doherty	Method (a)—Operated at normal rate, damper set for maximum cooling, no radiation shields on burner, inlet water 10° F below room temperature, outlet water at room temperature.	660
Doherty	Method (b) [a]	655
Doherty	Method (c) [a]	652

[a] See text.

9. PARR GAS CALORIMETER

Description.—This calorimeter, illustrated in Figs. 36 and 37, is of the comparison type, viz, the heating value of the gas under test is compared with that of a gas the heating value of which is known. In the Parr calorimeter the comparison of heating values is made by comparing the rise in temperature in two as nearly as possible identical calorimeters, in one of which the gas to be tested is burned, and in the other of which an equal volume, or a multiple or submultiple of this volume, of the gas of known heating value is burned, the gases being displaced under the same pressure from cylinders kept at the same temperature. The relative volumes of the two gases are chosen so as to cause, as nearly as possible, equal rises of temperature in the two calorimeters. Hydrogen is used as the gas of known heating value. If ordinary illuminating gas (600 Btu) is to be tested, then, since the heat of combustion of hydrogen is a little more than one-half that of the illuminating gas, two volumes of hydrogen are burned for each volume of illuminating gas. The calorimeter is provided with three similar gas cylinders of equal volumes, of which two may be connected in parallel, so that the ratios of volumes, 2 : 1, 1 : 1, and 1 : 2, may be obtained. These gas cylinders are contained in a water bath immediately under the pair of calorimeters. The gas is displaced from the cylinders by water from an elevated tank, so that the pressure on the two gases is the same if the water level in the gas cylinders is the same. The water levels in the gas cylinders are indicated on two gage glasses, and these levels, the differences of which at the beginning and end of a test determine the amounts of gas burned, are controlled by two needle valves, which are used to regulate the flow of gas to the burners. There is a needle valve above each of the gage glasses to permit the escape of air when the cylinders are filled with water, previous to drawing in the gases by running out the water, and to permit of adjusting the amount of gas in each cylinder, so that the water levels in the respective gage glasses shall be the same at the beginning of a test.

The calorimeters are two similar vessels of as nearly as possible equal capacities for heat. The water circulation in the two calorimeters is maintained by stirrers of the screw propeller type,

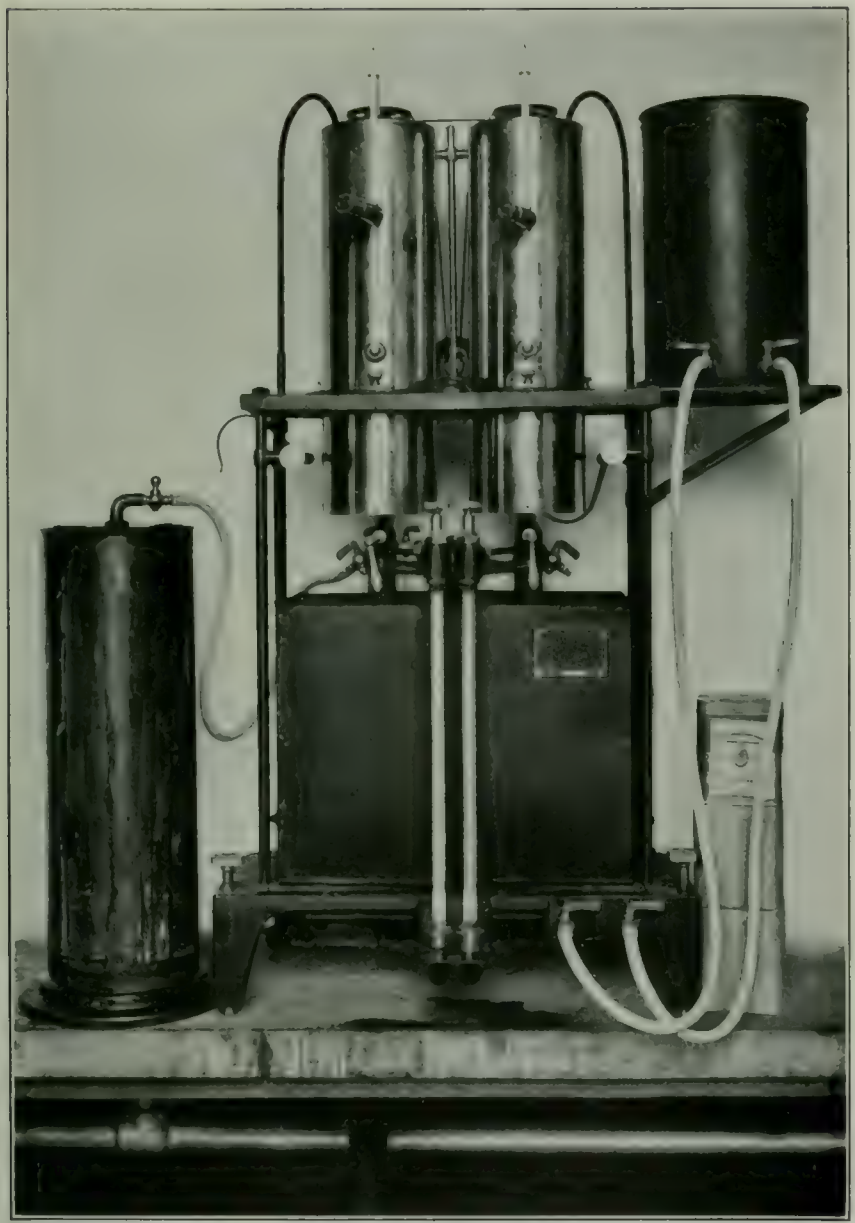

Fig. 36.—*Parr gas calorimeter*

the two stirrers being driven by a single belt from the pulley of a small motor. Each stirrer causes the water to circulate upward in a central tube, which is closed at the bottom, and which extends from about 1 inch below the surface of the water to within 3 inches of the bottom of the calorimeter. The water then flows

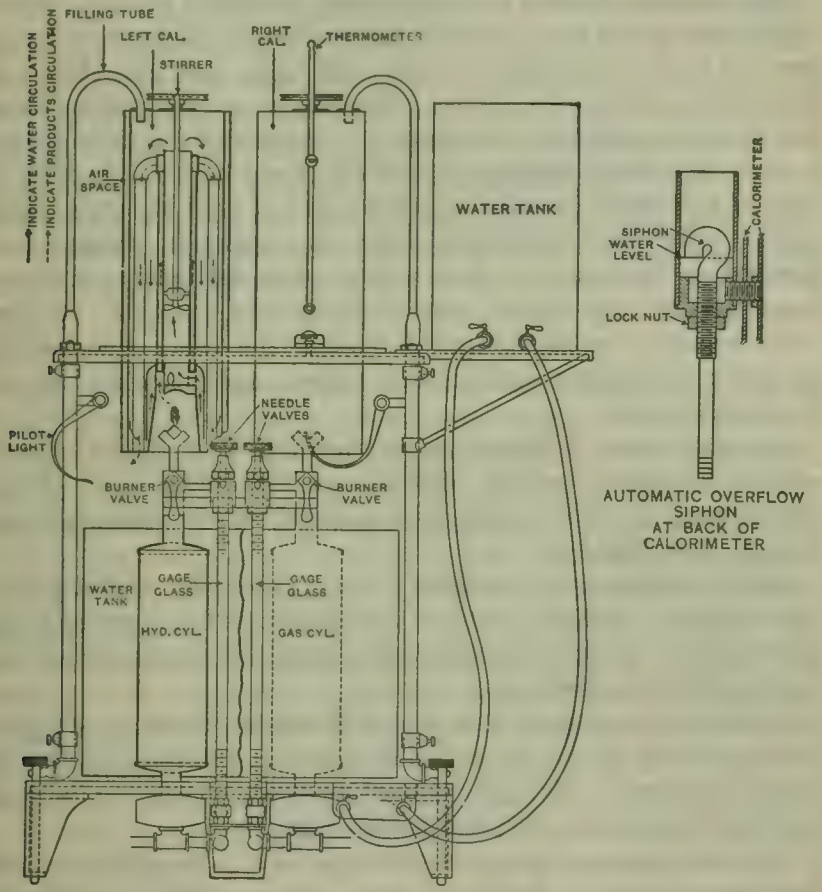

Fig. 37.—*Parr gas calorimeter (section)*

outward at the top and downward to the bottom of the calorimeter in an annular space in which is a set of condenser tubes to carry the descending products of combustion, thence upward a short distance around a partition and back into the lower portion of the central tube through three radial passages extending horizontally

across the combustion chamber. The level of the water in each calorimeter is determined by an automatic overflow siphon, which is adjustable so that the water equivalents of the two calorimeters can be adjusted to equality. The calorimeter stand is provided with leveling screws and with a circular spirit level.

The gases are burned in one-half foot acetylene burners, which are located in the lower parts of the respective combustion chambers. At the beginning of a test the gases are ignited at the burners by small pilot flames that can be momentarily turned into position under the calorimeters. The products of combustion in each calorimeter impinge against the closed bottom of the inner tube of the water circulation system and against the three horizontal radial water passages, then pass upward, through the interspaces between the three radial passages, into an annular space between the central water column and the outer annular water column, thence downward through the tubes immersed in the water of the outer annular water column, and out at the bottom of the calorimeter.

An angle stem thermometer is mounted in each calorimeter with its horizontal bulb in the outer annular water space of the calorimeter, the short horizontal portion of the stem passing through a stuffing box.

Each calorimeter is inclosed in an externally nickel-plated cylinder which incloses a narrow air space between itself and the calorimeter. Water connections are provided for renewing the water in the calorimeters.

Hydrogen is produced in a special generator shown in the photograph of Fig. 36, by the action of water on hydrone, an alloy of sodium and lead. The analyses that have been published indicate that the hydrogen so obtained is very pure.[27]

This calorimeter is not intended for and is not adapted to the determination of net heating values. No provision is made for collecting the condensate; indeed, some of the water condensed in the combustion chamber occasionally drops down on the burners.

In the use of this calorimeter care must be exercised to insure that the hydrogen delivered by the generator is not contaminated

[27] Report of Calorimetry Committee American Gas Institute 1912.

with other gases. Care must also be exercised to obtain an average sample of the gas to be tested and to avoid the introduction of air while filling the cylinders. In igniting the gas at the beginning of the test no gas should be allowed to escape unburned. If the gas does not ignite at the first trial, the cylinders must be refilled and the test started again. On account of the small volume of gas burned in a test the presence of even small leaks may cause appreciable errors. The results obtained in the determination of the total heating value of the same sample of gas with the Parr calorimeter and with the Junkers calorimeter (see Table 33) do not indicate that any appreciable error was introduced into the results obtained with the Parr calorimeter, due to the absorption of constituents of the illuminating gas by the water which displaced this gas or to the contamination of either the hydrogen or the illuminating gas by gases liberated from the water. No special experiments were made to directly test whether such effects existed.

The pilot lights can not be operated so as to produce heat at the rate of less than about 1 Btu per minute for each. The total amount of heat produced by the combustion of the gas in a test of illuminating gas is only about 30 Btu for each calorimeter. It is evident, therefore, that these lights should be made as nearly equal and as small as possible without danger of extinguishing them in use, and they should be so manipulated in lighting the gases that the difference in the amount of heat thus introduced under the one or the other of the calorimeters is negligible in comparison with the heat imparted to each calorimeter. For example, with pilot lights that produce 1 Btu per minute, if one of these lights were left under one calorimeter six seconds longer than the other pilot light, the difference in the amount of heat thus introduced under the calorimeters would be 0.1 Btu, which would introduce an error of about 0.3 per cent in the heating value found from the test.

The time required for a single heating value determination with the Parr calorimeter is probably not very different from the time required with a flow calorimeter. A series of determinations, however, can be obtained in considerably less time with a flow calorimeter.

The effect of slow deterioration in the heating value of illuminating gas, due to standing for a long time in the cylinders in contact with water, or the deterioration of samples which may be collected and subsequently tested, will depend upon the chemical constitution of the gas and is of the same nature as that discussed on page 98.

Special Tests.—The calorimeter tested, No. 2, was found to be in very good adjustment, with the exception that the volume of one of the three gas cylinders was about 2 per cent less than that of each of the other two. The volumes corresponding to one division of the gage glasses were determined for each gas cylinder and for the two cylinders in parallel, so that in case the position of the water in the two gage glasses was not the same at the end of a test the necessary correction could be applied. The weights of the two calorimeters, as well as their water contents, were found to be equal to within 0.1 per cent.

In all the experiments made with this apparatus calorimetric thermometers, inserted into the outer annular water spaces through openings in the tops of the calorimeters, were used instead of the angle stem thermometers mounted in the calorimeters, as there was some doubt as to whether the bulbs of the angle stem thermometers could be sufficiently immersed to avoid the effects of heat conduction.

The times of reading the initial and the final temperature of each calorimeter should be so chosen that the heat interchange with the surroundings in the interval between these times, due to conduction, convection, and radiation, is for each calorimeter proportional to the temperature rise in each. If the initial temperatures are so chosen that the final temperature of each calorimeter will be equal to the room temperature, the time elapsing between the initial reading and the ignition of the gas should be the same for each calorimeter. As under these conditions the final temperatures are practically stationary, the exact timing of the final readings is of little importance.

The application of the emergent stem corrections to the observed readings of the thermometers may be omitted, as the errors caused thereby are automatically almost entirely eliminated.

The equality of the heat capacities of the two calorimeters was tested by burning equal volumes of the same gas in each calorimeter. To eliminate the effects of residual errors in the thermometer corrections, which may be of importance on account of the small temperature rise obtained in this apparatus, the thermometers were interchanged after each test, the mean of two such tests being entered in Table 31 as the result of a single experiment.

TABLE 31

Rise in Temperature of Left and Right Calorimeters of Parr Gas Calorimeter When Equal Volumes of the Same Gas Were Burned in Each

Experiment No.	Left calorimeter	Right calorimeter	Ratio L/R
	°F	°F	
1	4.88	4.91	0.994
2	4.96	4.95	1.002
3	4.97	4.96	1.002
4	4.99	4.95	1.008
Mean	.....	.....	1.002

Although the observations were made with the greatest care, using accurately standardized thermometers graduated to 0°05 F, and eliminating residual errors of calibration by interchanging the thermometers, the precision of a single determination was not very great. However, if the two calorimeters are made thermally equal and the errors of the thermometers are eliminated by interchanging them, the variations among individual determinations are, to a large extent, due to accidental rather than constant errors, so that the mean of a number of determinations should be quite accurate. The above series of experiments shows that the heat capacities of the two calorimeters were equal to within the limits of precision attained in the use of the calorimeter.

To test the effect on the ratio of heating values found when the temperature rises of the calorimeters were quite different, the volume of gas contained in two of the gas cylinders was burned under the left calorimeter, while the volume of gas contained in one cylinder was burned under the right calorimeter, the initial

temperature of each calorimeter having been so chosen that the final temperature of each was approximately equal to the room temperature. The results of such a test are summarized in Table 32.

TABLE 32

Ratio of Temperature Rises in Left and Right Calorimeters when Volumes of Gas Burned were as 2/1

Experiment No.	Left calorimeter	Right calorimeter	L/R
1	9.89	4.92	2.010
2	10.01	4.93	2.030
Mean			2.020

The observations were made on a day of high humidity (80 per cent).

It will thus be seen that the ratio of temperature rises, which should have been 2:1, was about 1 per cent in error as determined by the calorimeter operated under the unfavorable conditions specified.

As it is not necessary, except in a few cases, to operate the two calorimeters with such different temperature rises, no special experiments were made to test the effect of atmospheric humidity under such conditions of operation.

The effect of variations in atmospheric humidity on the results is probably negligible when the calorimeter is operated so that the rise of temperature of the two calorimeters is nearly the same, but may become appreciable if the temperature rise of one calorimeter is considerably larger than that of the other.

Measurement of Total Heating Value.—The Parr calorimeter (No. 2) was applied to the measurement of the total heating value of illuminating gas. For this purpose the two gas cylinders of the left calorimeter were filled with hydrogen. The gas cylinder of the right calorimeter was filled with the illuminating gas to be tested, which was drawn from the 5 cubic foot gas holder. By means of a T connection, gas from the gas holder could be led either to the gas cylinder of the calorimeter or to a Bunsen burner. Before starting to fill the cylinder, a considerable volume of the gas

was burned in the Bunsen burner, which was also kept burning while the cylinder was being filled. The initial temperature of each calorimeter was so adjusted that the final temperatures attained were approximately equal to the room temperature.

The results summarized in Table 33 were obtained in the determination of the total heating values of two different samples of illuminating gas, with the Parr (No. 2) and the Junkers (No. 1209) calorimeters.

TABLE 33

Intercomparison of Parr and Junkers Calorimeters

Date	Parr calorimeter No. 2		Junkers calorimeter No. 1209
	Ratio illuminating gas/H	Btu of illuminating gas. H=321	
			Btu
Aug. 30, 1912, sample No. 1..	2.122	681	680
Aug. 31, 1912, sample No. 2..	2.137	[illegible]	[illegible]

The heating value to be assigned to the two samples of illuminating gas, as determined by the Parr calorimeter, will depend upon the heating value adopted for hydrogen. W. A. Roth[28] has recalculated the results of the more important determinations of the heating value of hydrogen. The mean of the five determinations summarized by Roth for the heat of combustion at constant pressure, of 1 mol of hydrogen, when the hydrogen and oxygen are initially at room temperature (70° F?) and when the water formed is condensed to liquid water at room temperature, is 68700 calories. This is equivalent to 321 Btu per cubic foot of hydrogen, saturated with water vapor, and measured at 60° F and 30 inches pressure. Parr has used the value 325 Btu per cubic foot, calculated from Thomsen's value, 68360 calories per mol. The value 325 Btu evidently applies to Thomsen's value for dry hydrogen measured at 60° F and 30 inches pressure. If the total heating value ordinarily desired, viz, for gas saturated with water vapor and measured at 60° F and 30 inches pressure, is to be determined, the heating value of hydrogen measured under the same conditions, must be used in the computations.

[28] Landolt-Bornstein-Roth, Physikalisch-Chemische Tabellen, Table 198a, p. 908.

In the Parr calorimeter, the ratio of the heating value of the gas tested to that of hydrogen is determined when both gases are measured under the same conditions of temperature, saturation, and pressure. This ratio is independent of the temperature and pressure prevailing in the test. If this ratio is multiplied by the heating value of hydrogen under standard conditions of temperature, saturation, and pressure, the resulting value will be the heating value of the gas tested under the same standard conditions.

The heat unit, in terms of which the results found with the Parr calorimeter are expressed, is the unit in terms of which the heat of combustion of hydrogen is expressed. No correction need be applied for the variation with temperature of the specific heat of water (or of the calorimeters).

X. SUMMARY

After an outline of the object of the investigation, precise definitions of the heat units and of the several heats of combustion are considered. After reference to the more important types of calorimeters that have been applied to the measurement of the heating values of gases, the principle of the flow calorimeter is set forth, and an example is given showing the reductions of and corrections to the observed data that are required in order to find the total and net heating values.

The results of an experimental investigation of laboratory gas meters, showing the errors to which such meters are liable, the precautions to be observed and the accuracy attainable in their use, are given at length. It is shown that an accuracy of about 0.2 per cent may be attained if the meter is calibrated in situ at the time of use, and that the calibration may be reproduced from time to time by making suitable adjustments, to within 0.5 per cent.

The results are given of an extended series of investigations of the various factors that may affect the accuracy of heating value determinations with flow calorimeters, such as: Completeness of combustion; accuracy of the temperature measurements; the magnitudes of the various heat losses from the calorimeter, particularly as affected by the volume of the entering air and of the

products of combustion and by the atmospheric humidity; and the accuracy of measurements of the quantities of water and of gas. The effects of certain other factors, which depend upon the nature of the gas tested and are particularly noticeable in the testing of illuminating gas, are briefly considered.

The results of an extended series of experiments with natural gas and with nearly pure hydrogen and with a mixture of the two gases having about the same heating value as ordinary illuminating gas show that, when the necessary corrections for losses of heat from the surface, for the effect of atmospheric humidity, etc., were applied to the observed heating values obtained with flow calorimeters of suitable design and construction, the total heating values thus found were in agreement to about 0.3 per cent with the total heating values obtained with calorimeters of the Berthelot bomb type, provided due allowance were made for the difference between the heat of combustion at constant pressure and the heat of combustion at constant volume.

The summarized results are given of a critical investigation of eight flow calorimeters, representing types widely used in this country or abroad, and of one calorimeter of the comparison type.

The investigation has shown that several of the calorimeters investigated could be used, when proper precautions were observed and suitable corrections were applied to the observed heating values obtained with them, to determine the total heating values of most kinds of gases to an accuracy of about 0.3 per cent. Some of the calorimeters are, however, subject to constant errors that can not be eliminated or be readily determined except by comparison with a standard instrument, such errors for one calorimeter amounting to nearly 2 per cent.

Examination of a very large amount of data obtained during the investigation indicates that with those calorimeters free from significant constant errors, total heating values should be determinable, under conditions obtaining in the industrial testing of gas, to an accuracy of the order of 1 per cent.

The methods of operation which this and other investigations have shown to be suitable for the various calorimeters are given in Bureau of Standards Circular No. 48 on Standard Methods of Gas

Testing in the form of detailed operating directions. The circular also contains other matters of interest in connection with the equipment of a calorimetric laboratory, as well as tables to be used in connection with heating value determinations.

The authors desire to express their appreciation of the assistance rendered by their colleagues throughout the investigation, among whom especial thanks are due to Messrs. H. C. Dickinson, D. R. Harper 3d, R. S. McBride, E. R. Weaver, and H. G. Barrott.

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IODINE NUMBER OF LINSEED AND PETROLEUM OILS

BY

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Bureau of Standards

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I. INTRODUCTION

The linseed oil used in the manufacture of printing ink is of the so-called "burnt" type. There are two general processes for its manufacture—one in which the oil is heated until the vapors take fire and continue to burn, the oil being allowed to burn until it attains the desired viscosity; and a second in which the oil is heated without permitting it to take fire.

Burnt oil is prepared in several grades, all differing from the raw oil in an increase of viscosity, specific gravity, and acid number, and a decrease in the iodine number. The longer the oil is heated the greater these differences become.

In the determination of the iodine value of some burnt linseed oils difficulty was experienced in obtaining concordant results. Leeds [1] has published some figures for iodine absorption of lithographic oils. Kitt [2] has also published a series of results which show decrease in iodine absorption with increasing viscosity, but the figures do not agree with those given by Leeds. These determinations were made according to the Hübl method.[3] In recent years this method has been so generally replaced by the rapid and more

[1] J. Soc. Chem. Ind., 13, p. 203; 1894.
[2] Chem. Rev. Fett. u. Harz Ind., 8, p. 40, 1901; J. Soc. Chem. Ind., 20, p. 40, 1901.
[3] Dingler's Poly. J., 253, p. 28-; J. Soc. Chem. Ind., 3, p. 641, 1884.

convenient Hanus [4] method that it was considered desirable to learn the values afforded by this method. Preliminary work developed the fact that small variations in the method employed produced varying results. It has been well established that iodine absorption includes not only the halogen taken up by unsaturated compounds, but that the substitution of halogen for hydrogen with the formation of halogen acid occurs simultaneously. Various methods for determining the amount of substitution have been suggested, with the view of obtaining a corrected value which would represent the addition only, but very little use has been made of them. It has been generally recognized that an excess of iodine is necessary, and it has been assumed that all oils are alike in the amount of excess required. The appended results obtained by us show that this is far from being true. Various quantities of iodine have been suggested as to the proper excess which should be present, but practically all of these are given in connection with discussions of the Hübl method, and may not hold true for the Hanus method. Furthermore, there has been a lack of uniformity in the use of the term "excess of iodine." In the tables which follow whenever this expression is used it shall be understood to mean that percentage of the total amount added which remains unchanged at the expiration of the time allowed for absorption.

II. PROCEDURE

The method employed was essentially the modification of the Hanus method suggested by Hunt.[5] Thirteen and two-tenths grams of iodine were dissolved in 1 liter of glacial acetic acid (99.9 per cent), and 3 cc of bromine added. This solution was always allowed to stand for some days before being used. The thiosulphate solution employed was approximately tenth normal, and was standardized by means of potassium bichromate. Standardization was repeated at frequent intervals. A freshly prepared starch solution was used; also a 10 per cent solution of potassium iodide, prepared in small amounts and kept in a brown bottle. The temperature of the room was maintained at 25° C

[4] Zs. Untersuch. Nahr. Genuss., 20, p. 913, 1901; J. Soc. Chem. Ind., 20, p. 1246, 1901.
[5] J. Soc. Chem. Ind., 21, p. 454; 1902.

to prevent variations caused by change of temperature. The reagents were of standard quality and errors caused by impurities were eliminated by running blanks with each series of determinations. When it was desired to use like amounts of an oil in a series of tests, 4 grams of the oil were dissolved in chloroform in a 200-cc graduated flask and the solution allowed to reach room temperature. Ten-cc portions of this solution, representing 0.2 gram of oil, were measured from a burette. The general procedure was as follows: The exact weight of oil was transferred to 250 to 300-cc glass-stoppered Jena bottles; the required amount of Hanus solution was added from a burette. The mixture was allowed to stand for exactly 30 minutes in a dark closet; 25 cc of the 10 per cent potassium iodide solution and 100 cc of water [6] were added,[7] and the excess of iodine was immediately titrated with thiosulphate.

The factors known to influence the iodine number are the temperature, the time of absorption, the weight of oil taken, and the excess of iodine present obtained by increasing the amount of iodine solution. The exact effect of each factor was studied by varying one at a time, this procedure being followed with a series of oils.

III. SAMPLES

The samples employed were as follows:

(*a*) A raw linseed oil, sample No. 3, of the four linseed oils tested by the American Society for Testing Materials [8] in 1909. This sample had been hermetically sealed, immediately upon completion of the tests in 1909, and had been kept in a cool dark closet.

(*b*) A boiled oil of the so-called "bunghole" variety.

(*c*) Four burnt linseed oils, Nos. 00, 1, 3, and 5. These oils were obtained from northwestern seed and, after refining, were heated in copper kettles at a temperature of 560 to 600° F until the desired consistency was attained.

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[6] Tolman and Munson: J. Am. Chem. Soc., 25, p. 244; 1903.

[7] Gill: "Oil Analysis," 6th ed., p. 62, footnote.

[8] See report of Committee E on Preservative Coatings for Structural Materials, Proceedings of the A. S. T. M., Vol. IX, p. 184; 1909, analyses by J. B. Tuttle. Another sample of this same oil was also tested in 1911, results of which are given in report of Subcommittee E of Committee D–1, Proceedings of the A. S. T. M., Vol. XI, pp. 23–30; 1911.

(*d*) Three petroleum oils. Two of these, marked light oil No. 1 and No. 2, were automobile cylinder oils, and the third was an engine oil. Upon analysis these oils gave the following figures:

	B. S. eng.	Light No. 1	Light No. 2
Flash	175°	220°	230°
Fire	210	265	280
Sp. gr. 20°/4°	0.9260	0.8738	0.9265
Carbonization (3 hrs. at 250°)	1.01%	0.11%	0.23%
Oxygen absorp. 144½ hours	1.60%	1.91%	1.90%
Original acidity (mg KOH, per g)	0.70	0.08	0.17
Acidity after exposure	13.52	14.39	13.83
Increase in acidity	12.82	14.31	13.66

The other constants of the samples were not determined, as they have no bearing on the present problem.

IV. RESULTS OF TESTS

TABLE 1

Linseed Oil

[Temperature, 25°; Time, 30 Minutes; 25-cc Hanus Solution; Weight of Oil Varied]

Oil	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Oil	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(a) Raw Oil					(a) Raw Oil—Continued				
0.0522	0.6669	0.0962	184.3	.....	0.6054	0.6669	0.6091	100.6	100.6
0.0522	0.6669	0.0970	185.8	.....	0.8013	0.6669	0.6191	77.3	77.3
0.0522	0.6669	0.0967	185.3	185.1	(b) Boiled Oil				
0.1044	0.6669	0.1940	185.8	.....	0.0600	0.6902	0.1066	177.6	.....
0.1044	0.6669	0.1955	187.3	.....	0.1181	0.6902	0.2102	178.0	.....
0.1044	0.6669	0.1949	186.7	186.6	0.1322	0.6902	0.2355	178.3	.....
0.1566	0.6669	0.2912	186.0	.....	0.1673	0.6902	0.2984	178.3	.....
0.1566	0.6669	0.2906	185.6	.....	0.2061	0.6902	0.3682	178.5	.....
0.1514	0.6669	0.2844	187.8	186.5	0.2220	0.6902	0.3962	178.4	.....
0.2004	0.6669	0.3735	186.4	.....	0.2523	0.6902	0.4438	175.7	.....
0.2004	0.6669	0.3746	186.4	186.4	0.2783	0.6902	0.4832	173.7	.....
0.2504	0.6669	0.4543	181.5	.....	0.2920	0.6902	0.4976	170.4	.....
0.2504	0.6669	0.4572	182.6	182.1	0.3217	0.6902	0.5250	163.2	.....
0.3027	0.6669	0.5098	168.4	.....	0.3328	0.6902	0.5346	160.6	.....
0.3027	0.6669	0.5098	168.4	168.4	0.3583	0.6902	0.5518	154.0	.....
0.4542	0.6669	0.5869	129.2	.....	0.3874	0.6902	0.5744	148.2	.....
0.4542	0.6669	0.5888	129.6	129.4	0.3969	0.6902	0.5848	147.4	.....
0.5008	0.6669	0.6071	121.2	.....	0.5550	0.6902	0.6344	114.0	.....
0.5008	0.6669	0.6103	121.9	121.5					

TABLE 1—Continued

Oil	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(c) Burnt Linseed Oil No. "00."				
0.1235	0.6811	0.1827	148.0	.....
0.1268	0.6811	0.1882	148.4	148.2
0.1465	0.6811	0.2154	147.0	147.0
0.1842	0.6811	0.2616	142.0	.....
0.1863	0.6811	0.2632	141.3	141.7
0.2539	0.6779	0.3401	133.0	.....
0.2506	0.6779	0.3297	131.6	132.3
0.3489	0.6779	0.4128	118.3	.....
0.3562	0.6779	0.4171	117.1	117.7
0.4490	0.6779	0.4658	103.7	.....
0.4497	0.6779	0.4658	103.6	103.6
0.6058	0.6779	0.5216	86.1	86.1
0.7831	0.6779	0.5583	71.3	71.3
(d) Burnt Linseed Oil No. 1				
0.0880	0.6787	0.1220	138.6	138.6
0.1891	0.6787	0.2480	131.1	.....
0.1917	0.6787	0.2512	131.0	131.0
0.2856	0.6787	0.3310	115.9	115.9
0.3577	0.6787	0.3788	105.9	.....
0.3595	0.6787	0.3796	105.6	105.8
0.4377	0.6787	0.4195	95.8	95.8
0.5853	0.6787	0.4753	81.2	81.2
(e) Burnt Linseed Oil No. 3				
0.1085	0.5846	0.1412	130.1	.....
0.1085	0.5846	0.1406	129.6	129.9
0.1632	0.5846	0.1962	120.2	.....
0.1632	0.5846	0.1948	119.4	119.8
0.2376	0.5846	0.2463	103.7	.....
(e) Burnt Linseed Oil No. 3—Contd				
0.2376	0.5846	0.2463	103.7	103.7
0.3264	0.5846	0.2937	90.0	.....
0.3264	0.5846	0.2944	90.2	90.1
0.4158	0.5846	0.3313	79.7	79.7
0.5346	0.5846	0.3612	67.6	67.6
0.6534	0.5846	0.3883	59.4	59.4
(f) Burnt Linseed Oil No. 5				
0.0517	0.5874	0.0671	130.0	.....
0.0517	0.5874	0.0668	129.2	.....
0.0517	0.5874	0.0682	131.9	130.4
0.1034	0.5874	0.1336	129.2	.....
0.1034	0.5874	0.1329	128.5	.....
0.1034	0.5874	0.1325	128.1	128.6
0.1551	0.5874	0.1858	119.8	.....
0.1551	0.5874	0.1858	119.8	119.8
0.2054	0.5860	0.2213	107.7	.....
0.2054	0.5860	0.2234	108.8	108.3
0.2423	0.5870	0.2468	101.9	.....
0.2423	0.5870	0.2464	101.7	101.8
0.2826	0.5870	0.2671	94.5	.....
0.2826	0.5870	0.2680	94.8	94.6
0.3634	0.5870	0.3016	83.0	83.0
0.4108	0.5860	0.3163	77.2	.....
0.4108	0.5860	0.3187	77.6	77.4
0.5249	0.5870	0.2883	66.8	66.8
0.6162	0.5860	0.3711	60.2	.....
0.6162	0.5860	0.3688	59.9	60.0
0.7268	0.5870	0.3810	52.4	52.4

TABLE 2

Linseed Oil

[Temperature, 25°; 0.2-g Oil; Time, 30 Minutes; Amount of Hanus Solution Varied]

Amount Hanus solution (cc)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Amount Hanus solution (cc)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(a) Raw Oil					(c) Burnt Linseed Oil No.				
20	0.4737	0.3258	162.9	.....	"00"—Con.				
20	0.4737	0.3271	163.6	.....	40	1.0816	0.2980	149.0	149.4
20	0.4737	0.3266	163.3	163.6	50	1.3520	0.3054	152.7	.....
25	0.5928	0.3619	181.0	.....	50	1.3520	0.3044	152.2	152.4
25	0.5928	0.3615	180.8	.....	60	1.6224	0.3052	152.6	152.6
25	0.5928	0.3609	180.5	180.8	70	2.0280	0.3066	153.3	.....
30	0.7114	0.3747	187.4	.....	70	2.0280	0.3060	153.0	153.1
30	0.7114	0.3754	187.7	187.6	(d) Burnt Linseed Oil No. 3				
35	0.8300	0.3822	191.1	.....	20	0.4622	0.1940	97.0	.....
35	0.8300	0.3820	191.0	.....	20	0.4622	0.1932	96.6	96.8
35	0.8300	0.3816	190.8	191.0	25	0.5778	0.2128	106.4	.....
40	0.9486	0.3831	191.6	.....	25	0.5778	0.2152	107.6	.....
40	0.9486	0.3806	190.3	191.0	25	0.5778	0.2152	107.6	107.2
50	1.1862	0.3832	191.6	191.6	30	0.6933	0.2284	114.2	.....
60	1.4235	0.3840	192.0	.....	30	0.6933	0.2282	114.1	114.1
60	1.4235	0.3824	191.2	191.6	40	0.9244	0.2444	122.2	.....
75	1.7793	0.3846	192.3	.....	40	0.9244	0.2438	121.9	.....
75	1.7793	0.3828	191.4	191.8	40	0.9244	0.2432	121.6	121.9
(b) Boiled Oil					50	1.1556	0.2488	124.4	.....
20	0.5522	0.3490	174.5	.....	50	1.1556	0.2488	124.4	124.4
20	0.5522	0.3472	173.9	174.2	60	1.3866	0.2518	125.9	.....
25	0.6902	0.3580	179.0	.....	60	1.3866	0.2506	125.3	125.6
25	0.6902	0.3574	178.7	.....	75	1.7334	0.2514	125.7	.....
25	0.6902	0.3560	178.0	178.6	75	1.7334	0.2506	125.3	125.5
30	0.8282	0.3606	180.3	.....	(e) Burnt Linseed Oil No. 5				
30	0.8282	0.3606	180.3	.....	20	0.4688	0.1966	98.3	.....
30	0.8282	0.3596	179.8	180.1	20	0.4688	0.1950	97.5	97.9
35	0.9662	0.3617	180.8	.....	25	0.5860	0.2148	107.4	.....
35	0.9662	0.3617	180.8	.....	25	0.5860	0.2140	107.0	107.2
35	0.9662	0.3617	180.8	180.8	35	0.8204	0.2440	122.0	.....
40	1.1044	0.3614	180.7	.....	35	0.8204	0.2424	121.2	121.6
40	1.1044	0.3619	180.9	.....	50	1.1720	0.2602	130.1	.....
40	1.1044	0.3634	181.7	181.1	50	1.1720	0.2584	129.2	129.6
50	1.3759	0.3639	181.9	181.9	(f) Burnt Linseed Oil No. 5[9]				
50	1.6510	0.3625	181.2	.....	20	0.4688	0.1804	90.2	.....
60	1.6510	0.3630	181.5	181.3	20	0.4688	0.1800	90.0	90.1
(c) Burnt Linseed Oil No. "00"					25	0.5860	0.1962	98.1	.....
20	0.5408	0.2640	132.0	.....	25	0.5860	0.1946	97.3	97.7
20	0.5408	0.2622	131.0	131.6	35	0.8204	0.2148	107.4	.....
25	0.6760	0.2820	141.0	.....	35	0.8204	0.2094	104.7	106.0
25	0.6760	0.2812	140.6	140.8	50	1.1720	0.2218	110.9	.....
30	0.8112	0.2992	149.6	.....	50	1.1720	0.2186	109.3	110.1
30	0.8112	0.2940	147.0	148.3					
40	1.0816	0.2996	149.8	.....					

[9] Temperature 0° C.

TABLE 3

Linseed Oil

[Temperature 25°; 0.2-g Oil; 25-cc Hanus Solution; Time of Absorption Varied]

Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(a) Raw Oil					**(d) Burnt Linseed Oil No. "00"Contd**				
5	0.5972	0.3284	164.2	.....	15	0.5606	0.2495	124.8	.....
5	0.5972	0.3281	164.1	164.2	15	0.5606	0.2486	124.3	.....
15	0.5972	0.3497	174.9	.....	15	0.5606	0.2501	125.1	124.9
15	0.5972	0.3495	174.8	.....	30	0.5606	0.2584	129.2	.....
15	0.5972	0.3493	174.7	174.8	30	0.5606	0.2579	129.0	129.1
30	0.5972	0.3629	181.5	.....	30	0.5606	0.2607	130.4	.....
30	0.5972	0.3625	181.3	.....	45	0.5606	0.2593	129.7	.....
30	0.5972	0.3616	180.8	181.2	45	0.5606	0.2586	129.3	129.8
45	0.5972	0.3677	183.9	.....	45	0.5606	0.2635	131.8	.....
45	0.5972	0.3680	184.0	184.0	60	0.5606	0.2614	130.7	.....
60	0.5972	0.3737	186.9	.....	60	0.5606	0.2642	132.1	.....
60	0.5972	0.3736	186.8	.....	60	0.5606	0.2628	131.4	131.5
60	0.5972	0.3733	186.7	186.8					
(b) Boiled Oil					**(e) Burnt Linseed Oil No. "1"**				
5	0.6811	0.3385	169.0	.....	5	0.5746	0.2310	115.5	.....
5	0.6811	0.3342	167.1	168.0	5	0.5746	0.2310	115.5	115.5
15	0.6811	0.3518	175.9	.....	15	0.5746	0.2405	120.3	.....
15	0.6811	0.3510	175.5	.....	15	0.5746	0.2436	121.8	.....
15	0.6811	0.3508	175.4	175.6	15	0.5746	0.2405	120.3	.....
30	0.6811	0.3548	177.4	177.4	15	0.5746	0.2440	122.0	.....
30	0.6811	0.3556	177.8	177.8	15	0.5746	0.2426	121.3	121.1
45	0.6811	0.3600	180.0	.....	30	0.5746	0.2500	125.0	.....
45	0.6811	0.3602	180.1	180.0	30	0.5746	0.2497	124.9	.....
60	0.6811	0.3602	180.1	.....	30	0.5746	0.2493	124.7	.....
60	0.6811	0.3592	179.6	179.9	30	0.5746	0.2496	124.8	124.9
(c) Boiled Oil[10]					45	0.5746	0.2540	127.0	.....
5	0.6760	0.3282	164.1	.....	45	0.5746	0.2519	126.0	.....
5	0.6760	0.3266	163.3	163.7	45	0.5746	0.2525	126.3	126.4
10	0.6760	0.3422	171.1	.....	60	0.5746	0.2540	127.0	.....
10	0.6760	0.3402	170.1	170.6	60	0.5746	0.2552	127.6	.....
15	0.6760	0.3466	173.3	.....	60	0.5746	0.2554	127.7	.....
15	0.6760	0.3462	173.1	173.2	60	0.5746	0.2559	128.0	127.6
30	0.6760	0.3490	174.5	.....					
30	0.6760	0.3506	175.3	174.9	**(f) Burnt Linseed Oil No. "3"**				
45	0.6760	0.3528	176.4	176.4	5	0.6691	0.2252	112.6	.....
60	0.6760	0.3528	176.4	.....	5	0.6691	0.2252	112.6	112.6
60	0.6760	0.3518	175.9	176.2	15	0.6691	0.2394	119.7	.....
(d) Burnt Linseed Oil No. "00"					15	0.6691	0.2374	118.7	.....
5	0.5606	0.2405	120.3	.....	15	0.6691	0.2402	120.1	.....
5	0.5606	0.2406	120.3	120.3					
15	0.5606	0.2509	125.5	.....					

[10] Temperature 0°

TABLE 3—Continued

Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(f) Burnt Linseed Oil No. "3"—Contd					(g) Burnt Linseed Oil No. "5"—Contd				
15	0.6691	0.2367	118.4	119.2	5	0.6689	0.2120	106.0	.....
30	0.6691	0.2472	123.6	.....	5	0.6689	0.2136	106.8	106.5
30	0.6691	0.2483	124.2	.....	15	0.6689	0.2309	116.9	.....
30	0.6691	0.2480	124.0	123 9	15	0.6689	0.2271	115.0	.....
45	0.6691	0.2532	126.6	.....	15	0.6689	0.2271	115.0	.....
45	0.6691	0.2532	126.6	.....	15	0.6689	0.2271	115.0	115.5
45	0.6691	0.2525	126.3	126.5	30	0.6689	0.2390	119.5	.....
60	0.6691	0.2539	127.0	.....	30	0.6689	0.2390	119.5	119.5
60	0.6691	0.2539	127.0	.....	45	0.6689	0.2411	120.6	.....
60	0.6691	0.2542	127.1	127.0	45	0.6689	0.2411	120.6	.....
(g) Burnt Linseed Oil No. "5"					45	0.6689	0.2425	121.3	120.8
					60	0.6689	0.2432	121.6	.....
5	0.6689	0.2145	107.3	.....	60	0.6689	0.2432	121.6	121.6
5	0.6689	0.2118	105.9	.....					

TABLE 4

Petroleum Oils

[Temperature, 25°; Time, 30 Minutes; 25-cc Hanus Solution]

Oil (grams)	Iodine absorbed (grams)	Iodine No.	Oil (grams)	Iodine absorbed (grams)	Iodine No.
(a) Light Oil No. 1			(c) Engine Oil		
			0.0202	0.0167	77.9
0.2313	0.0683	29.5	0.0418	0.0307	69.4
0.5896	0.1454	24.7	0.0644	0.0448	65.7
0.7542	0.1756	23.3	0.1312	0.0735	52.9
0.9222	0.2006	21.8	0.1683	0.0870	48.8
1.0322	0.2105	20.4	0.1932	0.0953	46.6
1.5037	0.2621	17.4	1.009	0.2202	21.9
2.3203	0.3288	14.2	1.059	0.2235	21.1
(b) Light Oil No. 2			1.167	0.2371	20.3
			1.203	0.2423	20.1
0.2381	0.0807	33.9	1.305	0.2516	19.3
0.5144	0.1363	26.5	2.069	0.3058	14.8
0.6800	0.1678	24.6			
1.0288	0.2145	20.9			
1.6731	0.2819	16.9			
2.5151	0.3429	13.6			

[Temperature, 25°; Time, 3 Hours; 25-cc Hanus Solution]

(d) Engine Oil			(d) Engine Oil—Continued		
0.2608	0.1328	50.9	1.169	0.2873	24.6
0.4382	0.1766	40.3	1.839	0.3474	13.5
0.8298	0.2391	28.8			
1.139	0.2854	25.0			

V. DISCUSSION OF RESULTS

TABLE 1

Table 1, the results of which are plotted in Figs. 1 and 2, show the difference in behavior of the various linseed oils when the amount of iodine solution added is kept constant and the weight of oil is varied. Fig. 1 shows the change in iodine number with increasing amounts of oil. The curves in Fig. 2 have been calculated from the data given in Table 1 to represent the change in iodine number with a decrease in the excess of iodine present. It will be of interest to compare these curves with those in Fig. 3. The striking point in this connection is the range in weight of oil over which the iodine number is constant in the raw and boiled oils, as compared with that of the burnt oils.

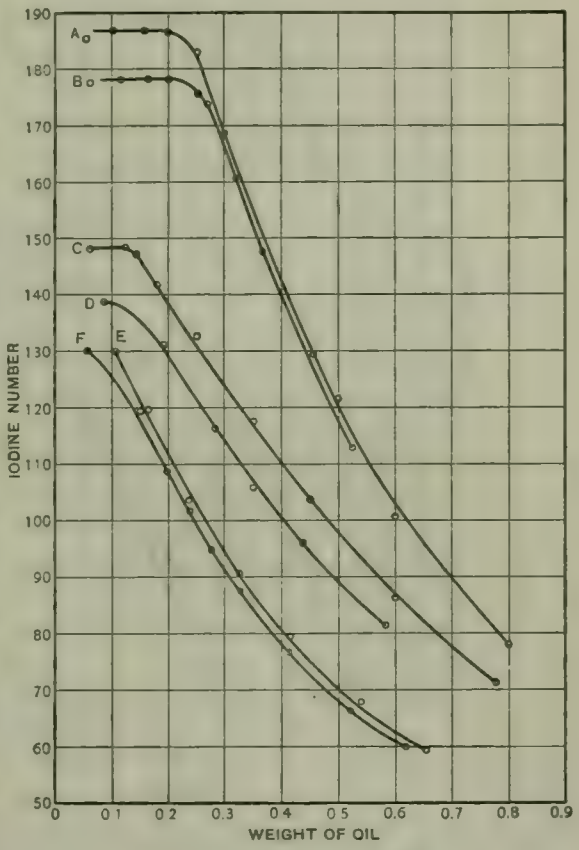

Fig. 1.—*Weight of oil varied*

It will be seen that, contrary to the general opinion, the oil with the highest iodine number does not require the largest excess of iodine to reach a maximum absorption value. It is not desirable to work with less than 0.1 gram of oil, because of the difficulty in obtaining constant values. Between 0.1 and 0.2 gram small varia-

tions in weight are negligible in raw and boiled oils, but are important in the burnt oils.

It is apparent that substitution plays an important part in the reaction, and we will refer to this point later on.

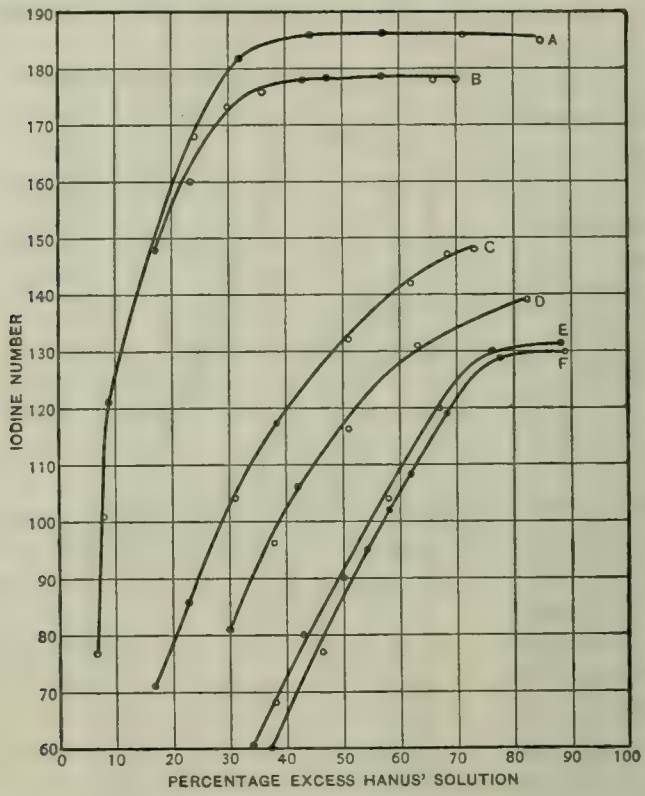

Fig. 2.—*Weight of oil varied*

TABLE 2

Table 2, in which the amount of Hanus solution is varied, is plotted in Fig. 3. Even more clearly than Fig. 2 does this show that burnt linseed oils do not readily reach a maximum.

The factor excess of iodine may be varied by changing the weight of oil or the amount of Hanus solution. In either case the effect upon the iodine number is about the same.

It is not sufficient, however, merely to specify the percentage excess of iodine, as the following figures, taken from Tables 1 and 2, will show:

Sample	0.1-gram oil 25-cc Hanus solution	0.2-gram oil 50-cc Hanus solution
Raw	186.4	191.6
Boiled	178.5	181.9
No. 00	139.5	152.4
No. 3	111.0	124.4
No. 5	109.0	129.6

These figures, together with the results shown in the preceding tables (1 and 2), demonstrate clearly that in these oils at least an iodine number should always be accompanied by full data as to the conditions under which it is determined, in order that it may be used for comparison.

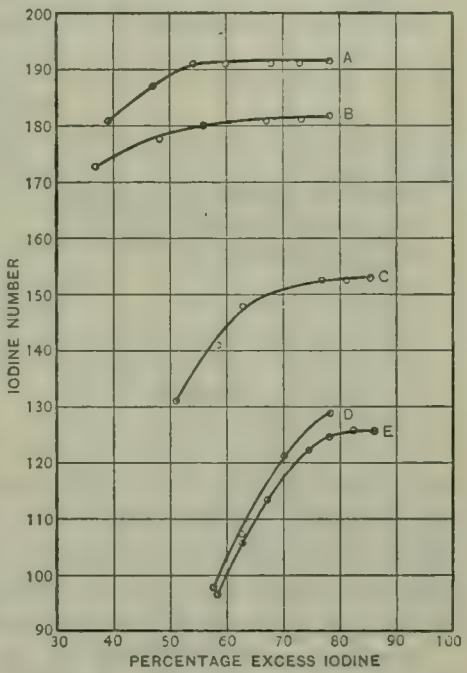

Fig. 3.—*Amount of Hanus solution varied*

When dealing with unknown oils it will probably be found satisfactory to determine the iodine value for several weights of oil, other conditions being held constant. For convenience we would recommend the use of 25 cc of Hanus solution and 30 minutes' absorption. When testing for the purity of a sample of oil a sample of known purity could be used as a standard, and by determining the iodine number on both samples under identical conditions adulteration or inferior quality should be readily detected.

The curve for Table 2 (*f*) will be found on Fig. 6, and will be referred to later. It is placed here so as to contrast it with the results given in Table 2 (*e*).

TABLE 3

The results of Table 3 (omitting (*c*)) are shown in Fig. 4. They show that after the first five minutes the absorption is slow, and the difference of a few minutes one way or the other after 15 minutes, will have little effect on the iodine value. Thirty minutes should prove a very satisfactory time and is now generally adopted.

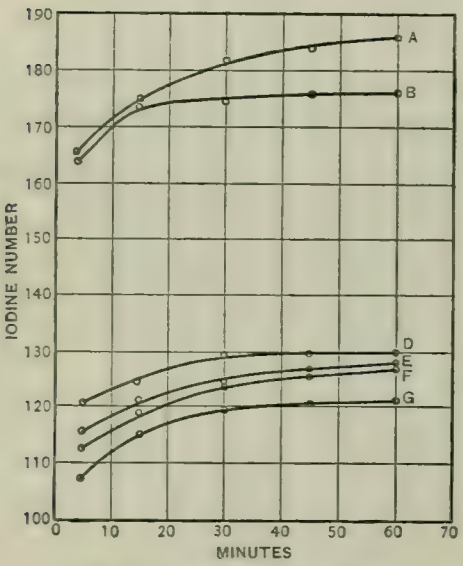

Fig. 4.—*Time of absorption varied*

Figs. 5, 6 contain two sets of curves showing the effect of temperature. Table 3 (*b*) and (*c*) show that, other conditions being equal, small differences in temperature at which an iodine value is obtained are negligible, so far as boiled oils are concerned, and presumably raw oils also, since their behavior is very much like that of the former. This is not, however, true of the burnt linseed oils, as inspection of the curves for Table 2 (*e*) and (*f*) will readily show. Using the largest practical excess of iodine, the difference between the results obtained at the two temperatures is too great to be considered negligible. Moreover, the fact that the curves are not even approximately parallel makes it difficult to allow for differences in temperature.

It will be seen that about 90 per cent of the absorption occurs in the first five minutes. If we assume that the addition of iodine is nearly instantaneous, and the substitution that part of the reaction which continues over a wide range of time, it is evident that any lessening of the time of absorption, which will at best eliminate only a small part of the total substitution, may give

low values which properly belong on the portion of the curve which is rapidly changing its slope.

A study of the effect of temperature on substitution is a more promising field than that of the time factor. Tables 2 (e) and 2 (f) as plotted in Fig. 6, show that at the lower temperature the effect of increasing the excess of iodine is less than at the higher one. The difference in the iodine values between 15 and 30 minutes is about 5 units (see Fig. 4), whereas the difference between 25° C and 0° C, at the maximum percentage excess of iodine employed, is 20 units. (See Fig. 6.)

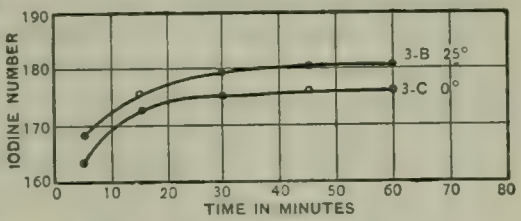

Fig. 5.—*Time and temperature varied*

TABLE 4

Fig. 7 shows clearly the futility of attempting to reach a constant value for mineral oils by increasing the excess of iodine. For the smaller quantities of oil used in the determination slight changes in the amount of oil taken cause large differences in the iodine number. Undoubtedly the lower values are more nearly correct than the higher ones, and therefore increasing the excess of iodine increases materially the error involved. To obtain concordant results the weight of oil and amount of iodine solution must be defined within very narrow limits. Our results indicate that not less then 1 gram of oil should be employed for the determination, with 25 cc of the iodine solution.

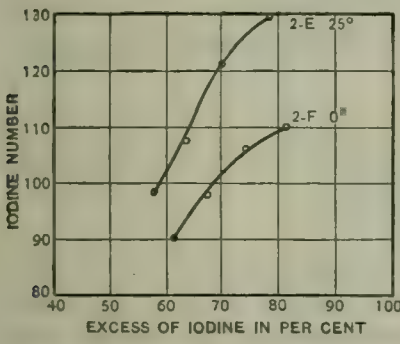

Fig. 6.—*Temperature and excess iodine varied*

It is interesting to contrast the behavior of linseed oils with that of mineral oils. The former tend to approach a constant value with a decreasing weight of oil, or increasing excess of iodine,

while, on the contrary, the latter tend to approach a constant value with increasing weight of oil.

VI. SUMMARY

The iodine values of raw, boiled, and burnt linseed oils were determined by the Hanus method, varying widely the amounts of oil and iodine used and the time of absorption.

It is shown that in order to obtain concordant results for iodine absorption a prescribed procedure must be followed exactly.

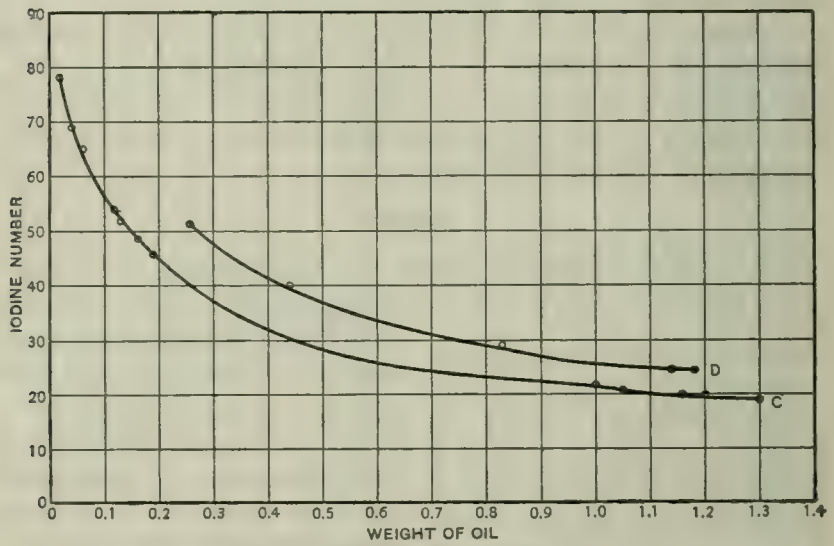

Fig. 7.—*Weight of engine oil varied*

To obtain comparable results a standard procedure should be adopted in which the limits are more exactly defined than is true at present. This is particularly necessary in the case of burnt linseed oils. With raw linseed oil a constant value is reached within comparatively wide limits of weight of oil and excess of iodine.

A study was made of the effect of temperature on the iodine absorption, from which it would appear that it may be feasible to improve the Hanus method by working at lower temperatures than those which have been used, and thus eliminate part of the substitution which occurs simultaneously with the addition.

The results obtained show that when used under exact conditions the Hanus method is to be recommended for simplicity of preparation of the solutions employed, ease of manipulation, and for concordance of results obtained.

Suggestions are made for the standardization of the method of determining the iodine number of mineral oils. The necessity for such action is shown by the results on several samples of lubricating oils.

We wish to express our appreciation of the courtesy of Messrs. Ault & Wiborg, of Cincinnati, Ohio, in furnishing us with the burnt linseed oils used in this work.

WASHINGTON, April 28, 1914.

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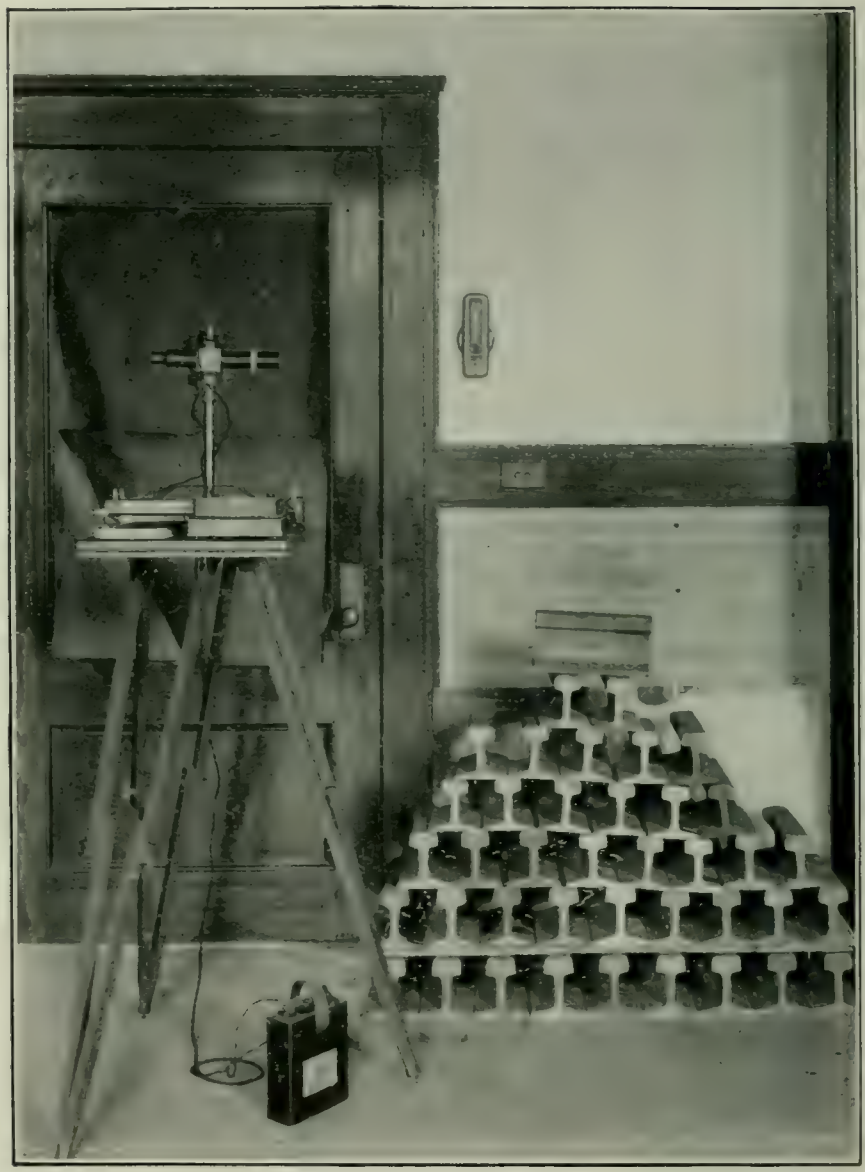

Fig. 1.—*Portable pyrometer outfit*

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

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No. 38

OBSERVATIONS ON FINISHING TEMPERATURES AND PROPERTIES OF RAILS

BY

G. K. BURGESS, Physicist
J. J. CROWE, Assistant Physicist
H. S. RAWDON, Assistant Physicist
and
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Bureau of Standards

[APRIL 28, 1914]

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By G. K. Burgess, J. J. Crowe, H. S. Rawdon, and R. G. Waltenberg

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1. INTRODUCTION

The dean of American metallurgists, Prof. H. M. Howe, in his presidential address before the American Society of Testing Materials in 1912, sounded a timely note of warning as to the responsibility of those societies and organizations which draw up model specifications. Said Prof. Howe:

> We set up standards for rails. It is strongly suspected and at times asserted that the breakage of these rails causes many needless deaths. If these rails are bought under our specifications, and if those specifications do not fully secure the very least attainable danger of breakage, we, as the experts on whose judgment these rails have been permitted, through their breakage, to kill our fellowmen, are in a measure responsible.
>
> The question thus seems to resolve itself into these: First, is there a considerable number of rail breakages capable of prevention by means of better specifications? Second, can we contribute directly or indirectly toward bettering these specifications by directing attention to their present defects?

It is common knowledge that there are an alarming number of failures of rails in service on the railroads of the country, and, unfortunately, these failures are not on the decrease. Thus the reports of the rail committee of the American Railway Association [1] show 36 641 rail failures, in 12 688 714 tons laid, for the year ending October 31, 1911, and 61 047 failures for 13 736 956 tons in 1912.

It is natural, on the one hand, for the rail manufacturer to claim that the railroads, with their increased speed and weight of trains, are mainly responsible for this condition, and that the rails now made are better than ever before; and, on the other hand, for the railroads to claim that the fault lies mainly with the rail manufacturer, who might furnish a sounder product. With the many deplorable and still unsettled aspects of this very vital question this paper makes no pretension of dealing.

That the railroads and rail manufacturers appreciate the gravity of the situation and the necessity of producing sound rails is shown by the fact, among others, of the introduction in some instances of a more comprehensive inspection system in the mills on the part of the railroads. As reported by R. W. Hunt,[2] "a great number of heats have not been rolled into rails, which, under old conditions, would have gone."

There is one phase of the process of rail manufacture that has received attention from time to time and to which it seems worth while to call attention again. We refer to the problem of the most suitable temperatures of rolling and particularly of finishing rails.

We shall recall briefly some of the salient points in the history of American practice in this matter of finishing temperatures, as shown in the proceedings and specifications of the several engineering societies, discussing in this connection the shrinkage clause first suggested about 1900, by which it was attempted to define the allowable upper limit of the finishing temperature by specifying the maximum contraction of the rail after it leaves the rolls and is cut into lengths at the hot saws. The desirability of setting

[1] Bull. A. R. E. A., **15**, p. 161, 1913; **14**, p. 335, 1912.

[2] See R. W. Hunt: "The American steel rail situation," Bull. Am. Inst. Mining Engrs. No. 86, 1914, p. 251; "Recent developments in the inspection of steel rails," ibid., No. 72, December, 1912, p. 1487; "Discussion," p. 1571.

limits of temperature of rolling rails will be considered with some mention of the data and experiments bearing on this subject. A short discussion of suitable methods of measuring rail temperatures will also be included; and, finally, the present American practice will be illustrated by measurements on ingot and finishing temperatures as observed in four representative rolling mills. Accompanying these temperature observations will also be found some of the characteristic properties of steel-rail material, as illustrated by samples taken from rails, the rolling temperatures of which were observed, including determinations of their critical points by means of cooling curves, temperature distribution through rail section on cooling, microstructure, expansion, tensile strength, and hardness. It will also be shown that, admitting the desirability of temperature control, this may be accomplished in a convenient, reliable, practical, and inexpensive manner.

2. IMPORTANCE OF LIMITING TEMPERATURES OF ROLLING RAILS.

It seems to be generally recognized that the factor of greatest importance in the manufacture of rails is the making of sound steel ingots; but it is also recognized that, starting with sound ingots in the rolling mill, the quality of the rails produced will depend in a very considerable measure on the process of rolling, and in particular on the temperatures. The undesirable effects of rolling too cold and too hot were very early recognized, and have been stated many times by competent authorities, although it should be pointed out that there is not complete agreement or conclusive evidence regarding the effects of finishing rails too hot.

As usually given the argument, briefly stated, is as follows:

Rolling steel below the critical range distorts and weakens the crystalline structure, while rolling and finishing at too high temperatures above the critical range produces a coarsely grained steel which is weaker than the finer-grained structure obtained by doing work continuously on the rail down to the critical range, which usually lies between 650° and 750° C (or 1200° to 1400° F) for rail steels, and is rarely above 700° C (1300° F.).

The manufacturer prefers to roll his rails hot, as less power is then required to operate the mill and there is less wear and tear

of the rolls so that, in practice, fixing a lower temperature limit is of relatively less importance, although the results of too cold or uneven rolling should not be overlooked in framing specifications. It is also claimed that a rolling temperature only slightly above the critical range tends to produce mechanical defects in the rail which are absent with higher rolling temperatures.

It appears to be the general consensus of opinion that with the high carbon rails of heavy section, with their greater tendency to brittleness, now so generally manufactured, the necessity of more closely limiting the upper temperature of rolling is of greater importance than with the lower carbon rails of a few years ago. Nevertheless, an examination of the specifications generally in use for the purchase of rails in this country will show that there has been a tendency to raise rather than lower the allowable upper limit of finishing temperatures as defined by rail shrinkage, and the question arises, if Prof. Howe's admonition is well taken, whether this specification should not now be subject to revision, both as to its numerical value and as to the manner of its measurement. More experimental work will also have to be done before satisfactory specifications can be drawn as to finishing temperatures, and it would be highly desirable if one or more of the mills could make a series of a considerable number of rails (several thousand at least), similar in all other respects as possible but each series rolled at a definite well determined temperature. This would not be difficult of accomplishment, and a record of their behavior in the track could easily be kept.

3. METHODS OF MEASURING RAIL TEMPERATURES

Almost all known methods of pyrometry have been applied to the measurement of rail temperatures, but for the most part with indifferent success and usually, it would appear, attended by some skepticism on the part of the engineers responsible for rail manufacture, which skepticism has perhaps prevented the introduction of temperature control even in rail mills of which the management was convinced of the importance of controlling rolling temperatures.

The problem, however, appears to present no unusual difficulties from the pyrometric point of view, and can be solved satis-

factorily in several ways; and, if desired, the temperature control may even be made automatic and continuous with only occasional supervision.

What is desired is a measure of the actual temperature of each of the rail bars, either as they emerge from the finishing pass, or, perhaps better, if we assume a constant speed of rolling through the rail passes, a measure of the temperature of the blooms as they enter the rail mill. There may be some advantage in the latter procedure, due to the fact that it permits holding a bloom if too hot before entering the rail passes and discarding a bloom that is too cold; or, for mills which give the blooms a wash heat, or a reheat, it might merely be necessary to control the temperature of this reheating furnace and the shortest time the blooms may remain in it. In a continuous mill it would perhaps be preferable to control the ingot temperatures.

The present "shrinkage clause" in American specifications would appear to be an unsatisfactory way of gauging temperatures, for one reason, among others, that rails finished too hot can not be checked out until they are cold, and in the meantime several tons of rails may also have been rolled too hot. Practically, of course, the shrinkage has to be allowed for, at least approximately, for convenience in manufacturing.

It has also been strongly advocated to control rolling temperatures by microscopic examination of the cold rail section. Unquestionably the microscope is an indispensable instrument for deciding from examination of its structure whether a rail has been rolled at a suitable temperature, but it would appear to be impracticable to use the microscope to replace a pyrometric method for the actual measurement of rail temperatures, for much the same reasons that the shrinkage method should be rejected.

Attempts have been made to measure rail temperatures by a calorimetric method, such as immersing in water a piece cut from a rail bar at the hot saws. This method can hardly be recommended as a convenient one for ordinary mill practice requiring, in spite of its apparent simplicity, the very active participation of several persons. Its only apparent merit would be the hope that it might give the average temperature throughout a rail section,

but there are so many uncertain features here involved, such as the specific heat and loss of heat during transfer, for instance, to mention only two, that the method can not be considered other than crude, cumbersome, complicated, and costly.

The center of the head of a rail at the hot saws is undoubtedly hotter than the surface. (See sec. 11.) Bearing in mind, however, the tendency of present rolling-mill practice to roll rails hot, there is no present danger that a measurement of the surface temperature properly made will cause the rejection of rails as being too cold.

One of the earliest methods of measuring surface temperatures of rails, and one still advocated by some, was by means of the thermoelectric couple provided with various mechanical devices for thrusting it up to, and holding momentarily against the rail during its pause at the hot saws. This method can probably be made to give consistent and reliable results, but is subject to considerable uncertainties, not the least of which is the deterioration of the thermocouple. In general, contact methods of measuring surface temperatures are to be avoided when other suitable methods are available.

Fortunately, there are available at least two reliable and convenient methods based on the use of optical and total radiation pyrometers, which permit an exact measure of the temperature of a hot rail in motion, and possessing the further great advantage of not requiring any contact with the rail.

In general, an optical or a total radiation pyrometer, if calibrated to read correctly when sighted through a small opening into a clear furnace, will read low when sighted upon any substance exposed in the open. For the oxides of iron, however, the radiation from which is measured or observed in case of rail temperature measurement, this correction is small, being quite insignificant for any of the optical pyrometers using a single colored light and from 20° to 60° C for the total radiation pyrometers, the amount of this correction depending on the pyrometer and the rail temperature. Any given radiation instrument may readily be calibrated to give correct readings of rail temperatures, and allowance may also be made, if desired, for the hotter interior of the head which is usually

from 10° to 100° C hotter at the hot saws than the surface of the head of the rail, depending on weight and section. (See sec. 11.) Heavy scale will influence the pyrometer readings somewhat, especially for the total radiation instruments, causing them to read low, but it is probably safe to say that when the scale begins to cause serious trouble the rails are coming through the rolls decidedly too hot.

There are a considerable number of types of optical and radiation pyrometers available.[3] Of the former, the LeChatelier and Shore optical and Féry absorption pyrometers require no accessories, such as electric battery and ammeter, but contain a kerosene lamp, which is influenced by drafts. The Wanner pyrometer, or its improved form, known as Scimatco, is made in two ranges, 600° to 1100° C and 900° to very high temperatures; the former meets the requirements for rails except that one can not see the object sighted upon and the instrument has to be brought uncomfortably near the hot body. The Morse pyrometer, especially the German type known as the Holborn-Kurlbaum pyrometer in the small telescope form, is very convenient to use and exact to 1° or 2° C, has a range from 600° C up, and can be sighted on a railhead 50 feet or more distant. With any of these optical instruments, nearly instantaneous measurements may be taken—that is, in two or three seconds—with practice.

A simple, self-contained optical device suitable for a rough estimate of a definite temperature interval is the stereopyrometer, which may be so adjusted as to permit determining whether rails lie above, within, or below two arbitrarily fixed upper and lower limits of temperature. Another optical pyroscope is the instrument of Mesuré and Nouel, with which readings consistent to within 25° or 50° C may be obtained with practice.

Among the total radiation instruments may be mentioned the Thwing, Féry, Foster fixed focus, and the Féry spiral pyrometers, the last requiring no galvanometer but apparently slightly less constant than the others. All of these instruments may be made to give a continuous record. They all, in their present forms, require to be brought rather close to the hot body, but the galvanometer

[3] See "Optical pyrometry": Waidner and Burgess, Scientific Paper No. 11, 1904, Bureau of Standards; also Burgess and LeChatelier: "The measurement of high temperatures," 3d ed., 1912, Wiley.

or reading dial may be read at any desired distance and the recorder may be placed in the superintendent's office. The total radiation pyrometers may be clamped in position and do not require the intervention of an operator to obtain the temperature indications, as is the case with the optical pyrometers. On the other hand, with the total radiation pyrometers it is necessary to make sure that one has an instrument which will take up its final reading closely enough within five or six seconds.

From the above considerations concerning pyrometers and from a study of rolling-mill practice, it appears clear that if it be considered desirable to control the temperatures of rails during their manufacture, the problem may be easily and exactly solved by means of several types of optical and radiation pyrometer which have given excellent service in other technical fields, and also with very small cost of installation and maintenance.

We have dwelt at some length on this question of the availability of pyrometers suitable for measuring the temperatures of rapidly moving rails, mainly for the reason that considerable misapprehension and ignorance of this subject appears to be common among engineers acquainted with rolling-mill practice. This attitude is well illustrated by the following quotation published within a year, which might have been excusable 10 years ago:

> The control of the finishing temperature by the amount of contraction which the rail undergoes in cooling from the finishing to atmospheric temperature, appears to be the only method practical to use. Other efforts have been made to determine the finishing temperature by the use of pyrometers and by the examination of the microstructure of the rails. The use of pyrometers naturally suggested itself at first as the most promising means of accomplishing that purpose, but it was soon found that no pyrometric device existed which could be applied in a practical way to the detection of the temperature of quickly moving rails.[4]

A similar statement appears in the 1911 edition of Harbord and Hall's "Steel."

We hasten to add that this pessimistic impression concerning the availability of pyrometers is by no means general as is illustrated, for example, by the investigations of Puppe,[5] who used the Wanner and Holborn-Kurlbaum instruments and of Wick-

[4] W. H. Sellew: "Steel rails," etc., published by Van Nostrand Co., 1913.

[5] J. Puppe: Ueber Versuche zur Ermitteilung des Kraftbedarfs an Walzwerken Berlin, 1909. (See also Iron and Steel Institute, I, 1912.)

horst,[6] (see sec. 4) who used the Thwing radiation pyrometer. The Féry instruments are also in use occasionally in several rolling mills.

4. WICKHORST'S EXPERIMENTS

M. H. Wickhorst[7] made an investigation of the influence of finishing temperatures on the properties of 85-pound Bessemer rails, using five ingots rolled, or rather finished, at temperatures ranging from 938° C to 1028° C, as measured with a total radiation pyrometer. The ingot temperatures were not measured and the blooms were reheated before rolling into rails, according to the practice of the Edgar Thomson Works.

No very definite conclusions as to the effect of rolling temperatures on the properties of rails can be drawn from this series of experiments covering only a 90° range in temperature, the lower temperature limit being close to the maximum allowed by present American specifications, as defined in terms of shrinkage, and higher than the upper limit allowed for example in 1905 by the American Railway Engineering Association. It is to be regretted that this investigation did not include rails finished at least as low as 800° C (1472° F) and as high as 1150° C (2102° F).

In spite of no marked influence detectable within this narrow range of finishing temperatures on the ductility, deflection and number of blows in the drop test, yield point, and tensile strength, Mr. Wickhorst apparently found a slight decrease in elongation and reduction of area with increase in finishing temperature, and a notable increase in size of grain.

The measurements of Mr. Wickhorst on shrinkage and temperature permit an approximate calculation of the mean coefficient of expansion of Bessemer steel of 0.49 per cent carbon and 1.10 manganese content. Although the temperature (t_c) at which the length (l_c) of the cold rails was measured, is not given, we may assume in the formula for expansion coefficient $\alpha = \frac{l - l_o}{l_o(t - t_o)}$ in which t is the finishing temperature of hot rail of length l, that

[6] M. H. Wickhorst: "Influence of rolling temperature on properties of Bessemer rails," American Railway Engineering Association Report 21, November, 1911.

[7] M. H. Wickhorst. Ibidem.

this length l_c is equal to l_o the length at 0° C; this is equivalent to adding a legitimate, small correction to the readings of the total radiation pyrometer used, which we know gives readings that are somewhat low when sighted on exposed objects.

In the accompanying table are given the results of these computations of the expansion coefficient.

Calculation of Expansion Coefficients from Wickhorst's Data

Finishing temperature	Shrinkage	Length of rail, cold		α_{0-t}
°C	Inches	Feet	Inches	
938	$6\frac{5}{16}$	33	$\frac{5}{16}$	0.0_4168_1
963	$6\frac{9}{16}$	33	$\frac{1}{16}$	170_4
990	$6\frac{11}{16}$	32	$11\frac{3}{16}$	173_9
1028	7	32	$11\frac{9}{16}$	172_1
1023	7	32	$11\frac{9}{16}$	

Mean value of $\alpha_{0-983°} = 0.0_4171_1$.

This value of the expansion coefficient α is considerably higher than that found by the authors for Bessemer steels, for which $\alpha_{0-1000°C} = 0.0_4146$ (see sec. 12) and also for open-hearth steels ($\alpha_{0-1000°C} = 0.0_4157$). To reduce Wickhorst's expansion results to those for Bessemer steel requires adding nearly 200° C to his temperature measurements. This correction is not beyond the bounds of possibility; since it is shown, for instance (sec. 11), that the outside of the head of a rail may be over 100° C below the temperature of the middle of the head while cooling; and in addition the correction to the radiation pyrometer used by Mr. Wickhorst will be over 50° C for lack of "blackness" of the iron oxide (see sec. 3); and finally if the Thwing radiation pyrometer is held too far away its readings will be lowered further due to the radiation not filling completely its aperture.

It is, of course, also conceivable that the Bessemer rails, as they leave the rolls, have the very high expansion coefficient deduced from Mr. Wickhorst's observations on shrinkage. Further experiments are necessary to demonstrate this. (See also sec. 12.)

5. MEASUREMENTS OF INGOT AND FINISHING TEMPERATURES

These were made in the spring of 1913 at four representative rail mills,[8] designated by A, B, C, D. The portable pyrometer used, the Holborn-Kurlbaum type of the Morse instrument,[9] is shown in Fig. 1 with samples cut from the rails. Temperature observations were taken by sighting on the rail bars at the instant of cutting by the hot saws, the pyrometer being located so as to view the head of the rails at the first saw, except for mill C, at which, for convenience, the base of the rails was sighted as they passed to No. 1 bed. Since mill C was rolling a rail of heavy base, the measurements are comparable with those made by sighting on the heads. That such was the case was also shown by direct observations. The only considerable element of non-uniformity of the measurements at the several mills lies in the fact that the distance and time from the finishing pass to the hot saws is not the same for the several mills. This time for mill D is about half that for mills A, B, and C, while the ratio of distances is, roughly, A = 4, B = 5, C = 3, and D = 1 for the positions at which temperature measurements were taken. Two of the mills, A and B, used one saw and the others four saws. For the former it was possible to measure the temperature of practically every rail, while for mills C and D the average temperature of the rail bar as it passed to be cut (for mill D, and after cutting for mill C) was measured. In mills A and B the blooms were not reheated and in C and D they were reheated before rolling into rails.

Measurements were also made at each mill of a series of ingot temperatures, observations being taken as the ingot entered the blooming mill and for each alternate pass. It was possible in some cases to take observations on rail bars from ingots the rolling temperatures of which had also been measured. Auxiliary temperature measurements were also made at mill A, including observations at the bloom shears, open hearth, Bessemer, and blast furnaces, before and during tapping, pouring into ingot molds,

[8] The names of the mills are not published, due to objection from one of them.

[9] See Waidner and Burgess: "Optical pyrometry," Scientific Paper No. 11 of Bureau of Standards, 1904.

and temperature of ingots at stripping and removing from soaking pits. These last will be published elsewhere.

In the following tables, 1 to 16, are given the measurements taken in the several mills. All observations were taken without any interference with the regular operation of the mills, and no special arrangements or installations were found necessary for manipulating the pyrometer.

MEASUREMENTS AT MILL A

TABLE 1

Temperatures of Successive Ingots Passing Through Blooming Mill With Times Taken to Pass Through

[Each temperature is the average of all taken (5 to 10) on each ingot]

Number of ingot	(a) Ingots [10] for 75-pound Bessemer rails		(b) Ingots for 100-pound open-hearth rails	
	Temperature	Time	Temperature	Time
	°C	secs.	°C	secs.
1	1138		1117	119
2	1138		1085	116
3	1136	111	1101	135
4	1134		1063	127
5	1132	90	1082	170
6	1138	95	1069	132
7	1122	101	1058	
8	1127	92	1076	123
9	1165	96	1093	138
10	1158	103	1062	120?
11	1144	110	1070	95
12	1160	109	1051	135
13	1139	139	1069	150
14	1121	134	1071	123
15	1124	108	1071	97
16	1159	161	1076	80
17	1152	161	1088	130
18	1139	96	1123	96
19	1152	179	1121	
20	1135	150		
Mean	[11] 1140±10	120±25	1082±16	121±16

[10] These ingots had been an unusually long time in the soaking pits.

[11] The sign ± refers to the agreement of ingot temperatures and not to the accuracy of temperature measurements, which last is about 5° C.

TABLE 2

Sample Detailed Observations on Ingot Temperatures at Blooming Mill, Showing Precision of Method

Ingots	Temperature	Ingots	Temperature
(a) Bessemer ingots:	°C	(b) Open-hearth ingots:	°C
No. 2	1133	No. 4	1100
	1135		1083
	1152		1094
	1147		1076
	1135		1052
	1123		1070
			1064
Mean	1138	Mean	1063
No. 6	1147	No. 7	1085
	1147		1076
	1123		1064
	1123		1082
	1129		1051
	1147		1059
			1076
Mean	1138	Mean	1068
No. 10	1182	No. 14	1064
	1152		1076
	1135		1084
	1147		1088
	1158		1064
	1158		1040
	1164		1064
Mean	1158	Mean	1069
No. 16	1170	No. 20	1124
	1158		1130
	1170		1124
	1176		1124
	1147		1111
	1147		1111
	1176		
	1135		
Mean	1159	Mean	1121

TABLE 3

Temperatures of End of Bessemer Blooms Under Shears, on Freshly Cut End

Temperature	Temperature
°C	°C
1170	1194
1200	1186
1194	1209
1190	1176
1205	1175
1212	1200
1200	1190
1212	1203
1194	1141
1192	1144

Mean = 1189 ± 15.

The values given are the average of the two or three cuts observed for each ingot.

The interior of the bloom, the temperature of which is here measured approximately, is at a somewhat higher temperature than the surface.

TABLE 4

Temperatures of 75-pound Bessemer Rails at Hot Saw

[Each reading represents a rail. Brackets are used to tie rails in same ingot]

Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails	Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails
°C	°C	°C	°C	°C	°C
916	909	900	956	947	931
922	...	903	926 [14]	916	903
928 [13]	916	903	928	916	...
890	903	890			
			913	909	913
916	926	903	916	925	890
909	909	891			
			929	926	916
894 [12]	903	888	928	917	909
890 [12]	875	...			
			909	928	...
926	922	893	928	909	896
916	890	...			
			922 [13]	921	896
909	909	...	928	928	900
926	909	...	928	930	913
918	916	900	922	914	900
953	941	...	896	890	...
947	931	903	928	903	877
928 [13]	922	913	941	931	931
890	877	871	922	916	877
947	965	953	921	938	928
950	928	934	956	917	896
943	941	941	Mean = 924 ± 13	918 ± 13	906 ± 15
941	928	922			

[12] Test-piece top. [13] Test-piece middle. [14] Test-piece bottom.

TABLE 5

Temperatures of Open-Hearth and Bessemer 90-pound Rails at Hot Saw

[Brackets tie rails from same ingot]

Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails	Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails
°C	°C	°C	°C	°C	°C
[15] 978	991	...	966	975	...
[15] 996	963	...	976	965	951
991	981	...	976	965	...
966	924	...	966	940	928
[16] 947	978	...	958	958	942
[16] 978	947	...			
1001	999	...	[16] 991	971	...
970	953	...	[16] 976	955	941
1003	982	...	963	955	...
969	951	...	968	964	940
974	975	...	991	991	...
1000	966	928	978	969	951
981	957	...	976	940	...
978	955	938	980	963	941
976	950	956	Mean = 976±10	964±12	942±7
[16] 966	954	...			
[16] 958	951	...			

[15] Open-hearth heat. [16] Bessemer new heat.

TABLE 6

Temperatures of Open-Hearth 100-pound Rails at Hot Saw

[Brackets tie rails from same ingot]

Temperatures of A and C rails	Temperatures of B and D rails	Temperatures of A and C rails	Temperatures of B and D rails	Temperatures of A and C rails	Temperatures of B and D rails	Temperatures of A and C rails	Temperatures of B and D rails
°C	°C	°C	°C	°C	°C	°C	°C
916	898	1017	984	970	968	997	991
916	890	980	959	972	942	991 [17]	[18] 959–896
953	932	1029	1003	1003 [17]	991	1005	997
953	938	1004	967	984	963	991	964
928	905	1025 [17]	996	982	971	Mean=	
900 [17]	876	1004	966	981	952	988±23	962±24
1013	997	1025	1000	1005	989		
966	928	1009 [17]	988	1001	970		
1015	993	1021	1002	1001	977		
991	943	1001	957	991	[18] 968		
1013 [17]	989	982	973	1018	1001		
991	953	981	948	972	947		

[17] Test piece. [18] Discarded.

MEASUREMENTS AT MILL B

TABLE 7

Measurement of Temperatures of Ingots for Open-Hearth Rails at Blooming Mill

Temperature	Time	Temperature	Time	Temperature	Time	Temperature	Time
°C	Seconds	°C	Seconds	°C	Seconds	°C	Seconds
1102	...	1085	111	1104	92	1091	87
1096	88	1057	105	1091	93	1095	95
1086	88	1092	97	1121	87	1095	90
1091	86	1088	118	[19] 1135	100	1121	84
1102	[illegible]	1102	94	1130	91	1109	82
1096	100	1094	107	1132	91	1100	85
1093	106	1100	99	1120	97		
1101	93	1110	91	1107	102		

Mean temperature=1102° C±12; mean time=91 seconds±7.

[19] New heat.

TABLE 8

Measurement of Temperatures of Head of Rail at Hot Saws for 72-pound Rails

A	B	C	D	Mean ABCD	E	F	G	H	Mean EFGH
°C	°C	°C	°C	°C	°C	°C	°C	°C	°C
954	942	942	936	941	954	943	926	896	930
966	953	948	928	948	965	945	919	898	932
956	955	943	917	943	954	931	919	902	927
956	945	926	929	939	952	944	920	906	928
966	960	943	932	950	960	...	922	905	929
948	945	940	929	945	954	940	920	901	929
943	931	918	914	927	...	...	...	...	...
...	...	...	...	...	948	933	918	908	919
958	951	937	929	944	948	929	918	894	922
962	923	920	917	928	940	920	908	894	915
942	934	922	908	912	940	920	902	878	904
922	912	908	887	907	926	906	894	872	902
922	909	899	897	907	912	897	882	866	889
926	917	905	907	912	926	908	902	882	904

TABLE 8—Continued

NEW HEAT

A	B	C	D	Mean ABCD	E	F	G	H	Mean EFGH
953	947	935	920	938	932	931	913	903	920
966	954	932	912	939	954	937	929	...	940
954	945	934	922	938	954	945	922	914	934
956	957	936	919	941	960	952	935	918	941
964	949	934	926	943	954	943	...	913	936
968	957	945	934	951	949	929	915	...	930
952	943	937	930	940	950	943	924	920	934
962	958	940	936	951	957	940	934	910	935
966	957	940	932	949	951	934	918	897	924
954	943	935	926	939	938	937	918	896	922
956	943	929	922	936	955	943	922	901	930
968	954	943	931	947	958	943	924	916	935
964	946	943	935	946	964	952	932	918	942
958	943	943	931	944	965	946	931	920	940
960	946	944	931	945	946	943	926	918	934
961	954	946	930	947	954	948	935	918	938
958	947	945	943	949	957	935	931	920	936
955	947	939	929	943	945	942	932	908	931
965	953	939	939	949	968	953	941	917	945
963	942	932	919	939	958	936	919	907	930
962	951	937	919	943	957	940	912	896	927
943	937	922	914	929	945	922	908	901	920
960	944	943	929	944	966	957	932	908	940
969	954	946	931	950	964	944	928	912	936
975	962	953	934	957	954	952	920	908	934
957	939	928	908	933	946	931	916	888	921
Mean 957±8°	945±9°	935±9°	923±9°	939±9°	951±8°	937±10°	920±9°	903±11°	928±9°

MEASUREMENTS AT MILL C

TABLE 9

Measurement of Temperatures of Ingots at Blooming Mill for 90-pound Rails

HEAT NO. X

Temperature	Time	Temperature	Time	Temperature	Time	Temperature	Time
°C	Seconds	°C	Seconds	°C	Seconds	°C	Seconds
1090	..	1091	66	1099	63	1104	73
1094	..	1091	69	1088	77	1072	76
1101	..	1114	71	1088	68	1094	..
1099	72	1108	68	1082	66		

TABLE 9—Continued

HEAT NO. Y

Temperature	Time	Temperature	Time	Temperature	Time	Temperature	Time
°C	Seconds	°C	Seconds	°C	Seconds	°C	Seconds
1104	..	1094	71	1060	72	1056	76
1121	71	1079	69	1072	70	1059	75
1132	71	1059	72	1060	..		
1100	71	1053	70	1055	73		

Mean temperature = 1087 ± 17° C; mean time = 71 seconds ± 3.

TABLE 10

Measurement of Temperatures of Base of 90-pound Rails Opposite No. 1 Bed Immediately Next Hot Saws

HEAT NO. X

Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails	Mean	Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails	Mean
°C	°C	°C	°C	°C	°C	°C	°C
899	902	890	898	923	920	902	915
902	906	898	902	922	916	901	913
899	899	907	901	929	917	903	916
920	910	884	905	910	905	898	901
920	910	884	905	906	902	...	903
906	896	881	894	909	906	878	897
912	912	895	906	896	886	882	888
926	912	892	909				

HEAT NO. Y

918	920	893	910	917	888	873	893
923	922	900	915	902	888	870	886
897	885	873	885	928	900	891	908
912	900	885	898	928	906	884	906
911	906	885	900	920	905	873	899
896	894	878	889	895	890	878	888
905	900	881	895	912	896	881	896
887	...	875	881	910	901	878	896
906	896	875	893	922	908	884	905
920	895	872	897	908	886	868	888
906	890	869	888	910	895	875	894
910	894	874	892	907	901	889	898
906	887	...	896				
916	896	866	893	**Mean** = 911 ± 8	901 ± 8	853 ± 8	899 ± 7
922	899	884	902				

TABLE 11

Rails from Reheated Blooms which had Previously Become Cold

Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails	Mean	Temperatures of A and D rails	Temperatures of B and E rails	Temperatures of C and F rails	Mean
°C	°C	°C	°C	°C	°C	°C	°C
931	922	905	920	931	921	908	920
920	905	882	902	931	922	908	921
918	908	893	907	935	931	921	929
917	908	897	908	930	912	...	921
938	924	909	928	922	920	897	914
924	921	905	916	929	920	912	920
931	931	909	924				
937	930	912	927	Mean=928±6	920±7	904±8	920±6
935	929	...	931				

MEASUREMENTS AT MILL D

TABLE 12

Measurement of Temperatures of Ingots for Rails at Blooming Mill

Temperature		Time	Temperature		Time
°C		Seconds	°C		Seconds
Heat No. a...	1074	..	Heat No. e...	1127	38
	1076	..		1144	35
	1088	34		1136	31
	1088	36		1110	38
	1097	..		1112	32
	1091	35		1111	36
	1112	..		1122	38
	1122	..		1123	38
Heat No. b...	1121	34	Heat No. f...	1114	41
	1111	36		1107	36
	1113	32		1104	36
	1112	39		1104	32
Heat No. c...	1106	..	Heat No. g...	1143	38
	1102	41		1144	35
	1088	..		1153	41
	1102	34		1146	33
	1105	..		1138	39
	1115	..		1125	49
Heat No. d...	1131	32		1125	37
	1117	41			
	1126	36			
	1124	37			
	1136	39			
	1128	34			

Mean temperature of all ingots=1118±15; mean time=37±2.3 seconds.

TABLE 13

Measurement of Temperatures of Head of 100-pound Bessemer Rails at Hot Saws

[Each reading is the average for a rail bar (two rails) before being cut. Time from last pass to station = 8 seconds; time for rail bar (two rails) to pass observing station = 8 seconds.]

Temperature	Temperature	Temperature	Temperature
°C	°C	°C	°C
1043	1056	1045	1030
1066	[illegible]	1037	1044
1047	1045	1043	[illegible]
1056	[illegible]	1045	1053
1056	1047	1043	1037
1039	1048	[illegible]	1034
1048	1057	1047	[illegible]
1054	1053	1056	1049
[illegible]	1057	1044	1023
1053	1034	1043	

Mean = 1047 ± 8° C.

TABLE 14

Measurement of Temperatures of Head of 100-pound Open-Hearth Rails at Hot Saws

[Each reading is the average for a rail bar (two rails) before being cut. Time from last pass to station = 8 seconds; time for rail bar (two rails) to pass observing station = 8 seconds.]

Temperature	Temperature	Temperature	Temperature
°C	°C	°C	°C
980	993	1000	1004
1019	992	[illegible]	998
988	999	[illegible]	[illegible]
968	[illegible]	[illegible]	1011
956	1009	991	[illegible]
953	[illegible]	974	[20] 1005
959	982	975	991
[20] 998	[illegible]	[illegible]	988
[illegible]	951	1005	972
[illegible]	[illegible]	1019	980
[illegible]	[illegible]	1021	982
[illegible]	[illegible]	1021	991
[illegible]	[illegible]	[illegible]	
991	1015	[illegible]	

Mean = 992 ± 15° C.

[20] New heat.

TABLE 15

Summary of Ingot Temperatures at Blooming Mill

Mill	Ingots observed	Average temperature	Average time in blooming mill	Remarks
		°C	Seconds	
A	20	1140±10	120±25	Excessive time in pits
	19	1082±16	121±16	In pits 1 hour 35 minutes to 2 hours
B	30	1102±12	91±7	Two heats
C	29	1087±17	71±3	Do.
D	43	1118±15	37±2.3	Seven heats

TABLE 16

Summary of Rail Finishing Temperatures

Mill	A			B	C	D
Location of station	Hot saw				Cooling bed No. 1	Just before hot saws
Distance last pass to station	4			5	3	1
Number of rails	120	70	80	312	171	186
Weight of rails	75	90	100	72	90	100
Type of rail	Bessemer	O. H.	O. H.	O. H.	O. H.	Bessemer and O. H.
(Letters indicate location of rails in ingot)	A & D 924±13 B & E 918±13 C & F 906±15	A & D 976±10 B & E 964±12 C & F 942±7	A & C 988±23 B & D 962±24	A=957±8 B=945±9 C=935±9 D=923±9 E=951±8 F=937±10 G=920±9 H=903±11 Mean ABCD 939±9 Mean EFGH 928±9	A & D 911±8 B & E 901±8 C & F 883±8 2d series A & D 928±6 B & E 920±7 C & F 904±8	Mean of A, B, C, D Bessemer 1047±8 Mean of A, B, C, D O. H. 992±15

An inspection of the data shows that there is practical uniformity among the several mills for the rolling temperatures of ingots for steel rails. the range being from 1080° C (1975° F) to

1140° C (2085° F). With the exception of the Bessemers of mill D, rolled at an average temperature of 1047° C (1917° F), there is no very considerable difference among the finishing temperatures of the rails as observed at the hot saws for the several mills, the range being about 880° C (1615° F) to 990° C (1815° F); or, in other words, the four mills all finished their rails to within 50° C of 935° C (1715° F) on the average, excepting the Bessemers of mill D. This temperature of 935° C is 270° C (520° F) above the mean value, 665° C (1230° F), of the critical ranges of these rail steels. (See sec. 9.) As shown in section 11 on the distribution of temperatures within the head of a cooling rail, the center of the head is some 50° C (120° F) to 60° C hotter than the optical pyrometer reading at 935° C; therefore the center of the head is finished, on the average, at about 325° C (615° F) above the critical range for 100-pound sections.

The tables on finishing temperatures show several other facts of interest. For example, it is evident that it is a possible and easy operation to determine accurately the temperature of each rail length in succession as it arrives at the hot saw. (See in particular Tables 4, 5, 6, and 8.) From the measurements at mill A the relative temperatures of rails differing in weight of section, rolled from ingots having closely the same weights and temperatures, are shown. (See Tables 4, 5, 6, and 16.) Thus the average of the finishing temperatures of the top rails (A and D or A and C) for 100, 90, and 75-pound sections were, respectively, 988°, 976°, and 924°, and similarly for the others.[20a]

6. SAMPLES AND CHEMICAL ANALYSES OF RAIL STEELS

Samples from rails were taken as follows: Mill A, samples 1 to 6, open-hearth, 100 pounds, 7 to 12, Bessemer, 75 pounds; mill B, samples 13 to 23, Bessemer, 72 pounds; mill C, samples 34 to 40, open-hearth, 90 pounds; mill D, samples 24 to 28 and 33, Bessemer, 100 pounds, 29 to 32, open-hearth, 100 pounds.

In Table 17 are given the analyses, as determined at the Bureau of Standards, of several rails from each of the mills, together with

[20a] In June, 1914, additional measurements were taken in mill B, as follows: At hot saw on 100-pound open-hearth rails, average temperature = 948±7° C; at last pass, 1089±10° C; of blooms leaving the reheater, 1257±23° C. (This mill had installed reheater since the measurements of 1913.)

the corresponding heat analyses as furnished by the mills (in case of mill C the rail analyses were furnished). These samples are representative of the composition of the rails, the finishing temperatures of which were observed. Although there are discrepancies, some of them of considerable magnitude, the heat and rail analyses, in general, check fairly well; and Table 17 gives what may be considered as a representative picture of the accuracy to be expected from such analyses as made to-day on a technical basis. Four of the rails were also examined for segregation by taking analyses of head, web and base, the results indicating, in so far as any conclusion can be drawn from so few determinations, that the order of difference in composition throughout a rail may be as great as the difference between heat and rail analyses.

More extended experiments along these lines would be desirable; and, in this connection, the Bureau, in cooperation with a committee of the American Society for Testing Materials, is beginning a study of segregation in test ingots, and this will be extended to a more comprehensive comparison of analyses of heats and finished products.

TABLE 17

Chemical Analyses of Rail Steels

[O. H.=open hearth; Bes.=Bessemer; Ht=heat analysis at mill; Rl=rail analysis at Bureau of Standards; H=head; W=web; B=base, of rail; a=Ni and Co.]

Mill	Heat	Rail No.	Carbon		Sulphur		Phosphorus		Manganese		Silicon		Copper		Nickel		Chromium		Weight of rail
			Ht	Rl	Ht	Rl	Ht	Rl	Ht	Rl	Ht	Rl	Ht	Rl	Ht[a]	Rl	Ht	Rl	
A	O. H.	R 1H	0.64	0.63	0.040	0.032	0.018	0.017	0.77	0.67	0.075	0.037	.....	0.098	0.59	0.30	0.56	0.57	100
		R 1W		.60		.047		.021		.67		.047		.079		.24		.60	
		R 1B		.60		.033		.018		.67		.056		.107		.16		.53	
A	Bes.	R 7H	.43	.43	.065	.091	.056	.072	1.04	.84	.....	.020	.....	.139	.60	.20	.15	.13	75
		R 7W		.46		.051		.068		.75		.022		.112		.19		.17	
		R 7B		.44		.099		.072		.73		.022		.086		.09		.19	
A	Bes.	R 9H	.49	.47	.054	.055	.066	.070	.98	.89	.051	.032	.....	.085	.52	.22	.17	.17	75
		R 9W		.47		.058		.071		.92		.025		.148		.28		.17	
		R 9B		.46		.055		.069		.93		.040		.137		.34		.15	
A	Bes.	R 11	.49	.33	.054	.053	.066	.062	.99	.94	.051	.048	.....	.124	.52	.15	.27	.15	75
B	O. H.	R 22	.59	.63	.042	.042	.023	.027	.63	.67	.....	.101	.....	.109	.....	.10	.....	.10	72
B	O. H.	R 18	.55	.55	.032	.029	.024	.022	.80	.78	.....	.126	.....	.074	.....	.00	.....	.00	72
C	O. H.	R 34	.66	.70	.052	.057	.025	.025	.68	.72	.056	.079	.....	.026	.....	.00	.....	.01	90
C	O. H.	R 35	.65	.57	.032	.027	.018	.017	.67	.57	.056	.033	.....	.014	.....	.00	.....	.01	90
D	Bes.	R 28	.53	.49	.042	.037	.098	.087	.86	.86	.093	.099	.....	.011	.....	.03	.....	.00	100
D	O. H.	R 30	.62	.62	.036	.031	.025	.023	.66	.60	.154	.175	.....	.024	.....	.00	.....	.01	100
D	O. H.	R 32	.73	.69	.040	.036	.036	.033	.80	.73	.149	.144	.....	.008	.....	.00	.....	.01	100
D	Bes.	R 25	.44	.50	.051	.042	.092	.081	.76	.92	.098	.101	.....	.007	.....	.06	.....	.00	100

7. MECHANICAL PROPERTIES OF RAILS

In Tables 18 to 20 are shown the mechanical properties of rails from the several mills (see Table 17 for chemical analyses and mills), as measured by R. P. Devries, of this Bureau, on samples taken as indicated.

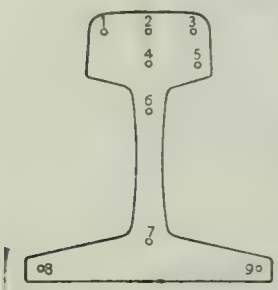

Fig. 2.—*Rail section, hardness survey*

An inspection of the tables shows a considerable variation in properties, especially hardness and ductility. The Brinell hardness numeral, as determined on the rail sections (Fig. 2), indicates in general a harder metal at the center of the head than for any other region of a cross section (Table 18). The values of the ultimate strength (Table 20) are quite uniform, and there is a somewhat less good agreement for modulus of elasticity (Table 19).

TABLE 18

Brinell Hardness Tests on Sections of Rail Parallel to Direction of Rolling

[Pressures applied by method of successive loading in the same indentation]

Rail No.	Hardness numeral [21] in kilograms; for positions—									Mean
	1	2	3	4	5	6	7	8	9	
R1	1025	1075	1034	1055	[illegible]	1213	1043	.....	1043	1061
R7	794	811	758	821	804	774	876	.....	[illegible]	811
R9	[illegible]	794	760	810	833	772	840	.....	732	791
R11	618	658	642	[illegible]	615	678	670	.....	[illegible]	657
R18	785	704	[illegible]	804	724	712	792	.....	787	764
R22	824	793	[illegible]	894	846	834	866	830	870	849
R25	768	712	752	746	704	682	758	682	705	723
R28	764	740	726	779	754	758	786	.....	764	759
R30	724	678	734	[illegible]	694	766	772	731	708	739
R32	[illegible]	[illegible]	852	848	778	880	862	.....	731	872
R35	756	810	780	805	757	779	774	.....	818	785

[21] Hardness numeral is the load in kilograms for 0.1 mm indentation with a steel ball of 10 mm diameter.

TABLE 19

Transverse Tests on Rail Specimens Taken from Flange

[Span 9"; section of specimen 1."25×0."37]

Rail No.	Modulus of elasticity (lbs. per sq. in.)	Fiber stress at proportional limit (lbs. per sq. in.)	Brinell hardness numeral in kg.	Rail No.	Modulus of elasticity (lbs. per sq. in.	Fiber stress at proportional limit (lbs. per sq. in.)	Brinell hardness numeral in kg.
R1	35 000 000	92 500	987	R24	29 680 000	71 700	653
R6	26 720 000	62 800	595	R31	30 020 000	73 800	904
R7	27 300 000	71 200	849	R32	27 900 000	44 800	946
R11	26 080 000	69 900	661	R33	24 600 000	64 000	592
R17	27 700 000	80 600	795	R34	26 400 000	73 300	860
R18	26 300 000	75 100	801	R39	33 100 000	69 400	830
R19	32 170 000	80 800	832				

TABLE 20

Tension Tests of Rail Specimens Cut from Head of Rails

Rail No.	Proportional limit (lbs. per sq. in.)	Yield point (lbs. per sq. in.)	Ultimate strength (lbs. per sq. in.)	Elongation in 2 inches in per cent	Reduction of area in per cent	Appearance of fracture
R1	56 000	66 500	126 500	17.5	36.6	Dull granular, 98 per cent Bright granular, 2 per cent
R7	40 000	56 600	112 000	21.5	40.2	Dull granular
R9	37 000	56 200	111 500	21.0	42.8	Dull granular interspersed with 5 per cent bright circular
R11	37 000	49 000	93 400	27.5	51.0	Dull granular
R18	41 000	50 500	106 200	23.5	38.8	Dull granular, 98 per cent; bright granular, 2 per cent
R22	.....	.....	113 000	9.5	8.3	Bright granular
R25	53 000	54 400	109 800	22.0	32.5	Dull granular, 65 per cent Bright granular, 35 per cent
R28	43 500	52 700	107 200	22.5	35.8	Inner circular section 50 per cent dull granular; outer circular section 50 per cent bright granular
R30	30 000	43 000	84 500	20.0	27.6	Dull granular, 30 per cent; bright granular, 70 per cent
R32	47 000	59 600	124 700	9.0	6.6	Bright granular; broke four times in threaded portion of specimen
R24	39 000	56 400	117 000	7.0	8.3	Bright granular
R35	35 000	46 000	104 500	19.0	27.1	Inner circular section 50 per cent dull granular; outer circular section 50 per cent bright granular

8. MELTING TEMPERATURES OF RAIL STEELS

The temperatures at which samples from several steel rails became completely liquid were determined in hydrogen by the method of the micropyrometer[22] and the melting and freezing ranges of two samples in hydrogen vacuum in the Arsem electric furnace. The temperatures as given in Table 21 are reported on the basis of the melting point of pure iron equals 1530° C (2786° F). Some of the irregularities in the table are probably due to lack of homogeneity, especially in the microscopic samples observed with the micropyrometer.

It is interesting to note that steel of the compositions used in rails, at least up to 0.75 per cent carbon, is not completely melted until the melting point of pure iron is nearly reached, 1530° C. Melting of these steels begins and freezing ends, however, in the neighborhood of 1470° C (2680° F).

TABLE 21

Melting Temperatures of Rail Steels

Rail No.	Kind of steel	End of melting with micropyrometer		Melting and freezing ranges	
		Observed	Mean	Melting	Freezing
R 24	Bess.	1510	1516		
		1520			
		1518			
R 32	O. H.	1530	1531	1478 to 1531	1527 to 1454
		1532		1485 to 1527	1533 to 1480
					1515 to 1445
					1531 to 1471
					1531 to 1475
R 40	O. H.	1525	1523		
		1522			
R 14	O. H.	1522	1522		
		1522			
R 22	O. H.	1519	1528	1482 to 1529	1527 to 1465
		1581			
		1533			
		1528			
R 6	O. H.	1527	1528		
		1530			
R 11	Bess.	1528	1525		
		1522			

[22] G. K. Burgess, "A Micropyrometer," Scientific Paper No. 198, Bureau of Standards, 1913; G. K. Burgess and R. G. Waltenberg, "Melting points of the refractory elements, I," Scientific Paper No. 205, Bureau of Standards, 1913.

9. CRITICAL RANGES OF RAIL STEELS

In Figs. 3 and 3*a* are given the first heating and cooling curves by the inverse rate method in vacuo, of samples from several Bessemer and open-hearth rails.[23] The ordinates are degrees centigrade and the abscissæ the number of seconds for the sample to change 2° C in temperature. Each dot represents an observation. The samples were of about 11 g contained within a nickel cylinder of 42 g. The beginning and end of a critical range is, in general, less well defined than its maximum.

In Table 22 are given the location of the critical ranges and rates of heating and cooling, together with the carbon and manganese content of the rails for all the observations taken. It will be noted that on heating all these steels develop a single, well pronounced critical range, the maximum of which, Ac123, is situated for all of them to within 7° C of 732° C (1350° F).

The cooling curves, which are of main interest, all show a very pronounced maximum, Ar1, between the limits 680° C (1256° F) and 650° C (1202° F) and some of the steels relatively lower in carbon show also the Ar23 range between 670° and 690° C. The difference between Ac1 and Ar1 is therefore of the order of 65° C (150° F).

From the thermal data, it follows that all these rails could have had work done on them then to advantage during the rolling process down to 700° C (1292° F), whereas for none of them was the actual finishing temperature lower than 880° C (1615° F).

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[23] The methods and apparatus for determining critical ranges are described at length in the following: "On methods of obtaining cooling curves," G. K. Burgess, Scientific Paper No. 99, Bureau of Standards, 1908; "Critical ranges A_2 and A_3 of pure iron," G. K. Burgess and J. J. Crowe, Scientific Paper No. 213, Bureau of Standards; and "The measurement of high temperatures," G. K. Burgess and H. LeChatelier, 3d ed., 1912, Wiley, Pub.

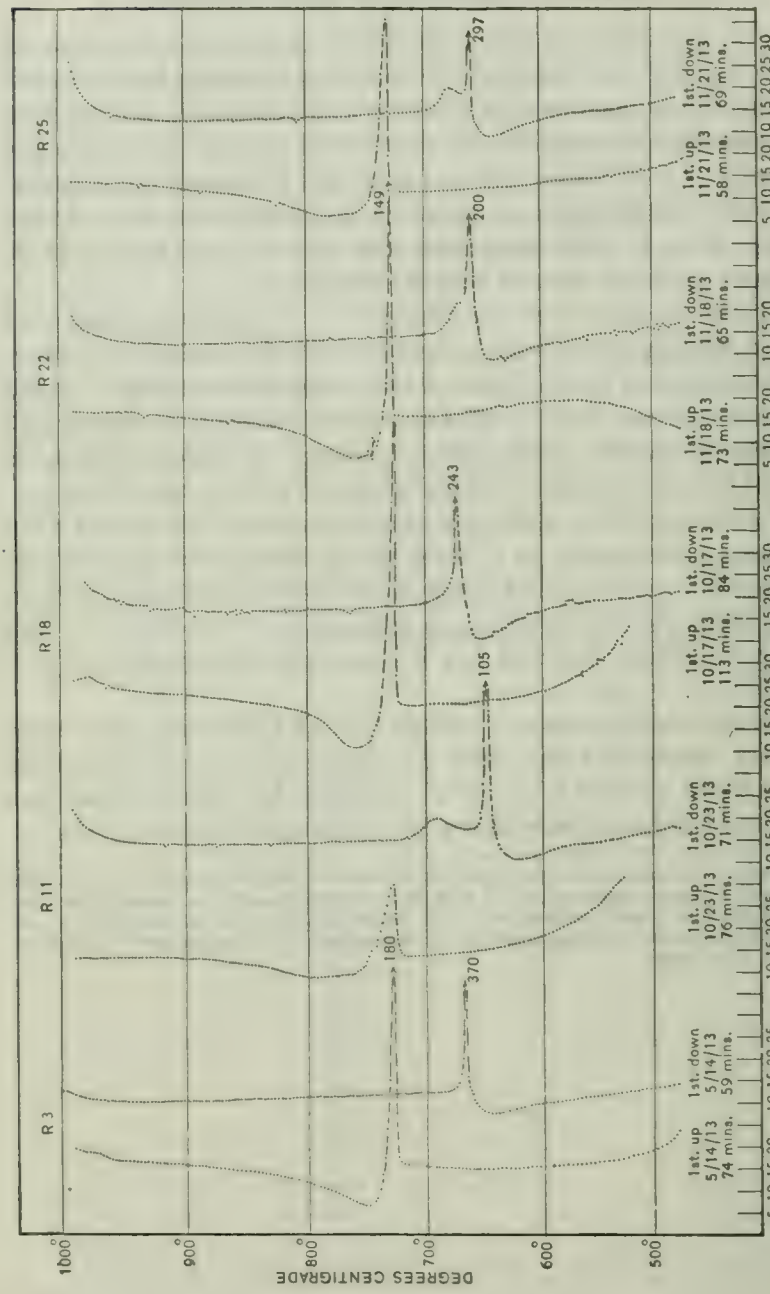


Fig. 3.—Cooling and heating curves of rail steels

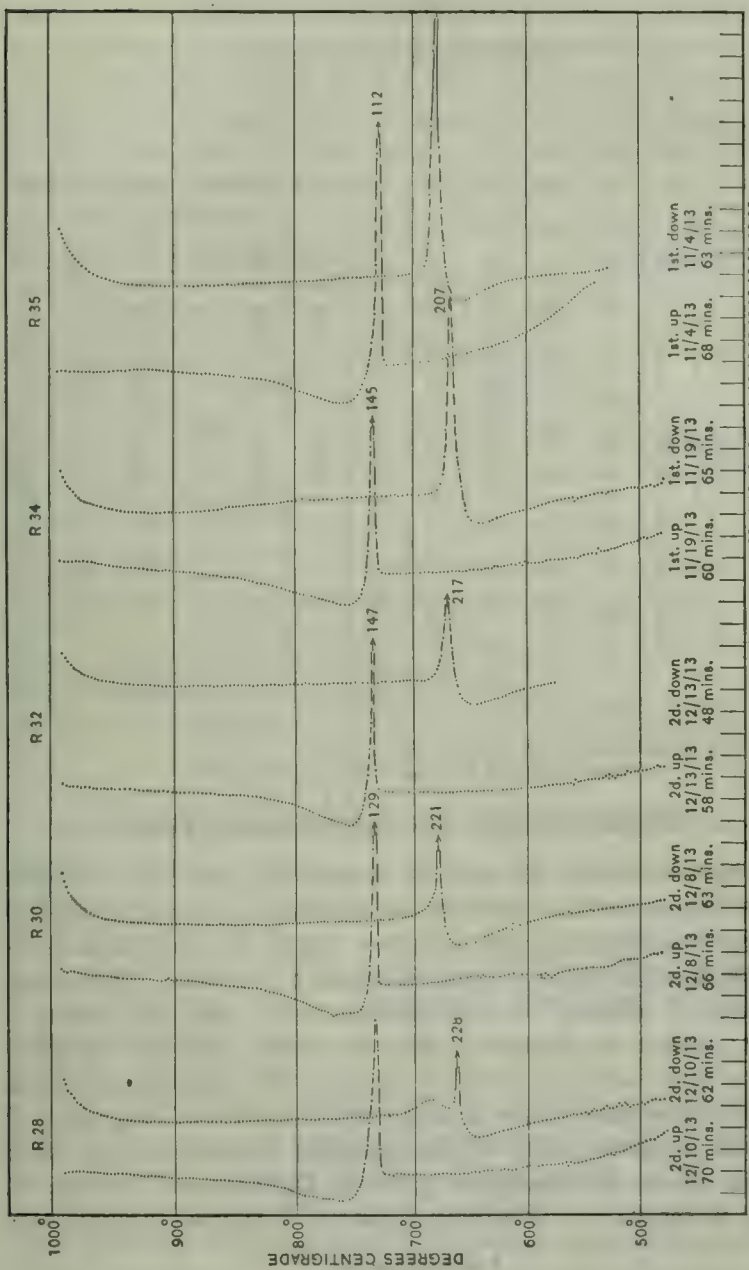


Fig. 3a.—Cooling and heating curves of rail steels

TABLE 22

Critical Ranges of Rail Steels

Rail No.	Analysis per cent		Rate—deg secs		Ac123			Ar23			Ar1		
	C	Mn	Up	Down	Begin	Max	End	Begin	Max	End	Begin	Max	End
R3	.....	.....	0.116	0.145	729	739	758	.....	.....	.....	691	675	653
R11	0.33	0.94	.113	.121	720	729	762	720	692	664	654	649	625
			.252	.156	730	736	.....	712	690	.....	649	648	.....
			.194	.139	726	733	742	708	687	659	659	655	645
			.108	.128	720	728	761	719	697	654	654	649	625
R18	.55	.78	.076	.102	720	726	757	.....	.....	.....	729	674	654
			.126	.133	727	729	.....	.....	.....	.....	693	673	.....
			[34].382	.125	720	734	758	.....	.....	.....	689	675	666
R22	.63	.67	.115	.132	726	728	742	690	672	658	668	662	647
R25	.50	.92	.148	.124	726	732	762	695	678	667	667	661	641
R28	.49	.86	.121	.136	726	732	766	690	672	660	660	649	630
			.....	.....	727	734	760	711	689	671	671	662	647
R30	.62	.60	.125	.134	732	734	748	.....	.....	.....	674	665	642
			.130	.136	729	732	748	.....	.....	.....	711	676	664
R32	.69	.73	.150	.132	729	732	748	.....	.....	.....	683	663	634
			.....	.....	730	734	751	.....	.....	.....	687	670	649
R34	.70	.72	.143	.132	725	732	748	.....	.....	.....	682	667	640
R35	.57	.57	.126	.136	725	727	757	.....	.....	.....	693	679	664
			.105	.084	[34] 725	731	757	.....	.....	.....	718	680	664
					[34] 729	731	744	.....	.....	.....	689	681	674

Mean location of maxima: (Ac123) 732°±5; (Ar1) 665°±7.

[34] Observations with Leeds and Northrup drum recorder.

10. OBSERVATIONS ON MICROSTRUCTURE [25]

The microstructure of steel is dependent upon the chemical composition, especially the carbon content, the heat treatment the metal has received, and, to a less extent, the influence of the mechanical work which is done in shaping the piece. Rail steel, in general, is allowed to cool undisturbedly after the rolling is finished so that the factor of heat treatment may be neglected. Fig. 4 is introduced in order to simplify the necessary explanations and references to the iron-carbon equilibrium diagram. It represents a portion only of the complete diagram and is taken from the report of committee 53 of the International Society for Testing Materials on "The nomenclature of the microscopic sub-

[25] By H. S. Rawdon.

stances and structures in iron and steel." No attempt is made to give the exact temperatures of transformation, and a few features have been added to illustrate the results of some of the work discussed. The line A1 is apparently too high.

Pure iron, like all solid metals, has a crystalline structure, though the crystals lack the definite geometrical form usually associated with this term. During the solidification of a metal, crystallization begins at a great number of points throughout the mass, and the shape of any individual crystal will depend upon its contact with neighboring ones. The addition of carbon, for the formation of steel, means the introduction of a new constituent into the microstructure. In low-carbon steels, the greater part of the metal is still pure iron, i. e., practically so; this is the ferrite and appears white after the ordinary method of etching. The second constituent, the pearlite, i. e., the one containing the carbon, is a mechanical mixture of two others, the ferrite and a definite compound of iron and carbon, Fe_3C, or cementite. Under low magnifications after the ordinary acid etching pearlite appears dark and homogenous. Examination under higher magnification shows that it is really a very finely laminated mixture of two

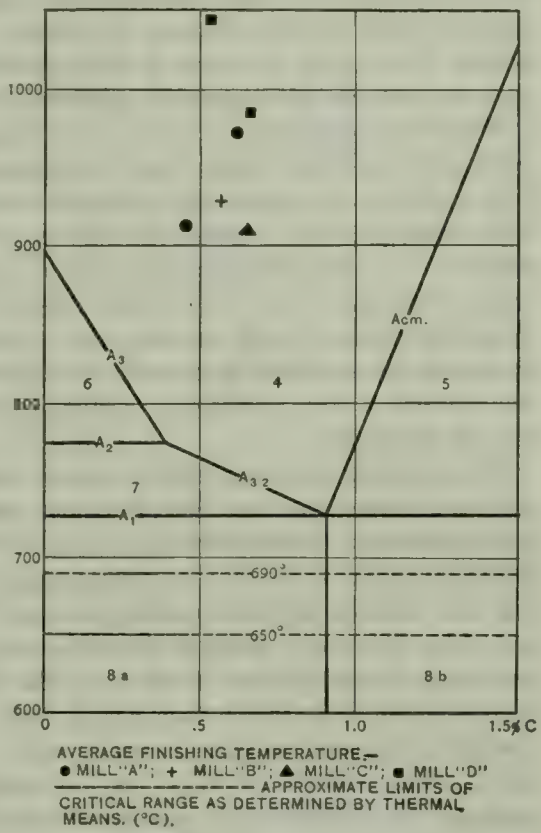


Fig. 4.—*Portion of iron-carbon diagram*

constituents which are alternate lamellæ of ferrite and cementite. As the percentage of carbon is increased the amount of pearlite correspondingly increases at the expense of the ferrite until at the eutectoid composition, about 0.85 per cent C, the whole mass is composed of crystals of pearlite. In steels having carbon contents of 0 to 0.85 per cent, the percentage of pearlite is directly proportional to the carbon content; in steels with a carbon content greater than 0.85 per cent a new constituent, free cementite, appears, and the percentage of pearlite correspondingly decreases.

When the temperature of any steel is raised above the transformation or critical range, i. e., it is represented by some point in area 4 of Fig. 4, the carbon exists in solid solution in the iron. This definite solid solution of carbon in iron, which is called Austenite, is crystalline and the size of crystals depends upon the temperature to which it has been raised above the critical, also upon the sojourn at this temperature. There is also an allotropic change in the iron itself in passing through the critical range so that the variety of iron existing in region 4 is entirely different from that in region 8a.

Upon cooling any steel with a carbon content between 0.00 per cent and something less than 0.85 per cent from a temperature corresponding to some point in area 4, the metal cools uniformly until the upper limit of the critical range is reached (A_3, A_{32} in Fig. 4). As the metal in cooling reaches the temperature represented by the proper point in this line, ferrite begins to precipitate out from the individual crystals of the austenitic mass and is ejected to the exterior of the crystal, thus forming a more or less complete wall or boundary for the crystal. This ejection of ferrite (iron) consequently enriches the remaining central nucleus in carbon. The process of ejection of iron or ferrite is continued until the temperature represented by the line A_1 (Fig. 4) is reached, at which temperature the remaining central austenite crystal has a carbon content of approximately 0.85 per cent, the eutectoid composition, and on further cooling changes bodily into a laminated mass of ferrite and cementite, i. e., pearlite. Further cooling is accompanied by no marked structural change.

Upon heating from below the critical range, the process is reversed as this range is passed through, i. e., the laminated

pearlite grain is changed bodily into a homogeneous solid solution of carbon in iron, austenite, as the lower limit of the transformation range is passed and, as the temperature continues to rise, more and more of the ferrite is dissolved until finally the solid solution of carbon in iron of the concentration corresponding to the carbon content, results as the upper limit of the critical range is reached. Above the eutectoid composition, a similar process goes on with the substitution of free cementite for ferrite as the constituent which is thrown off by the austenite crystal.

The grains of ordinary annealed steel of less than the eutectoid percentage of carbon consist therefore of a central mass of pearlite with a more or less definite boundary of ferrite. In steels of very low carbon content the amount of pearlite is so small that it is often mistaken for the boundary of the crystals of ferrite. Under certain conditions much of the ferrite which is expelled from the austenite during the cooling through the transformation range is retained within the cleavage spaces of the crystal of austenite and the ferrite network is consequently masked.

The study of the microstructure of the rails in question is largely limited to observations on and to measurements of grain size. The steels lie within a comparatively narrow range in carbon content, 0.33 to 0.73 per cent; all but five fall within the limits 0.45 to 0.66 per cent. The only prominent differences in microstructure are the amount of ferrite thrown out during cooling and the size of the crystals. Inasmuch as the investigation deals primarily with the temperature of rolling of the different steels rather than the method of manufacture, the occurrence and amount of impurities, "slag," etc., was not emphasized in the study of the microstructure.

Grain-Size Measurement.—The term "grain size," as ordinarily used to describe the fracture of steel, is a rather loose one and not clearly defined. As here used, in describing the microstructure, it is the number of pearlite grains or cells (with the accompanying ferrite boundary) per unit area of section (square inch). This is easily determined with an accuracy sufficient for the purpose by projecting the magnified image of the polished and etched specimen upon a ground glass screen ruled in inch squares. By means

of an accurately divided microscope slide, the linear magnification at any camera extension may be quickly determined by the direct measurement of the projected image of the divided scale. A linear magnification of 50 diameters was used; each square inch as measured on the screen represents, then $(0.02)^2$ square inch. The centers of the pearlite cells were indicated on the projection screen and the actual number per square inch is quickly calculated. In each rail measurements were taken at four different spots of each of the three samples—one each from head, web, and base—and the average taken for each. In computing the general mean for the rail, weights of 2, 1, and 2 were assigned to the grain count of head, web, and base, respectively, as these numbers represent very closely the relative areas of these three parts. The magnification used, 50 diameters, was found to be the best for general purposes. A lower magnification, e. g., 25 diameters, while giving a larger area for observation, makes the counting laborious and, in the case of the finer-grained steels, the difficulties in counting offset the increased accuracy due to the larger area. The specimens for microstudy were taken as illustrated in Fig. 5.

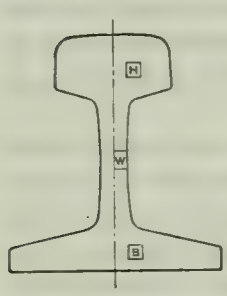


Fig. 5.—*Rail section, microstructure*

Relation of Temperature of Rolling to Microstructure.—The steel, as it comes to the rolling mill, is in the condition represented by a point in area 4 of Fig. 4, i. e., austenite. The effect of the various passes through the rolls is to crush and shatter the crystalline grains. At the temperature at which the rolling is carried on, the molecules of the metal have considerable mobility and consequently any distortion or disarrangement of crystalline structure is quickly repaired and the crystal begins to grow again in size until the next pass through the rolls repeats the distorting process. The latter passes, therefore, represent the temperature range which determines the size of the austenite crystals and subsequently the "grain-size" of the finished product. The nearer the temperature of the latter passes is to the upper limit of the critical range the smaller will be the austenite crystals and consequently the final "grain-size" of the steel.

If the rolling is continued down into the critical range, the microstructure of the finished rail will show this by the distortion of the ferrite which is precipitated in passing through this range. If rolling is carried on much below the lower limit of the range, the "pearlite-point," the distortion of both ferrite and pearlite crystals will record this fact.

The pyrometric observations upon the different rails during the process of rolling show that this process was finished well above the critical range of the steel. The microscopic examination confirms this in every one of the 40 rails. An examination of the photomicrographs given which illustrate the typical structure of the rails they represent shows that the ferrite outline of the pearlite grain has not been distorted or disturbed in the least after being formed. The rolling process with its attendant crushing and distortion of the crystalline structure of the austenite crystal has been completed before any ferrite appeared. In nearly all of the rails, the size of the pearlite cells indicate that the rolling process was discontinued at a temperature well above the upper limit of the critical range so that the crystal (then austenite) has time to reorient itself and grow to a fair size before any ferrite appeared. In Fig. 4 the average temperature at which the rolling was completed is indicated and, in all cases, is a considerable distance above the critical range as determined by direct thermal observations.

No definite conclusions can be drawn as to the relation of grain size and finishing temperature. The maximum difference in temperatures observed is approximately 135° C. Rails 1–6 of mill A and 34–40 of mill C, finished at approximately 908° C, are the coarsest of the series, but this large grain size may be the resultant of two important factors, high finishing temperature and large rail section, i. e., less "work" in rolling the stock.

The statement is sometimes made that the finishing temperature of rolled steel is equivalent to the highest temperature of objects heated but not rolled or forged so far as "grain size" is concerned.[26] The results here obtained do not seem to bear out this contention entirely. Though finished at a relatively high

[26] H. M. Howe: Proc. Am. Soc. Test. Materials, 11, p. 340; 1911.

temperature, the resulting structure is not to be described as excessively coarse. The average grain size of 29 rails in which a count could be made with certainty is 34 600 which is inclined toward the medium fine-grained rather than the extremely coarse.[27] The most striking variations from this mean value are rails Nos. 29, 38, and 40 (Table 23), in which both the head and base are coarsest of any observed.

TABLE 23

Rail No.	Mill	Wt.	Average finishing temperature	Kind	Mn.†	C.†	Number of grains per square inch			
							Head	Web	Base	Average
		Pounds	°C							
1	A	100	975±23	O. H.	0.67	0.61	(*C)	(*)	(*C)	(C)
2	A	100	975±23	O. H.	.67	.61	19 500	(*)	(*)	(C)
3	A	100	975±23	O. H.	.67	.61	(*)	(*)	(*)	(C)
4	A	100	975±23	O. H.	.67	.61	14 600	30 000	17 500	18 800
5	A	100	975±23	O. H.	.69	.59	(*C)	(*C)	(*C)	(C)
6	A	100	975±23	O. H.	.69	.59	(*)	(*)	(*)	(*)
7	A	75	916±13	Bess	.77	.44	43 100	40 300	28 600	36 700
8	A	75	916±13	Bess	.98	.49	33 800	53 500	43 900	42 000
9	A	75	916±13	Bess	.91	.47	19 800	25 700	17 700	35 700
10	A	75	916±13	Bess	.99	.46	11 900	38 200	43 700	29 900
11	A	75	916±13	Bess	.94	.33	30 700	44 500	48 200	40 500
12	A	75	916±13	Bess	.96	.43	18 700	29 700	41 300	29 200
13	B	72	934±9	O. H.	.78	.55	35 500	43 000	53 500	44 200
14	B	72	934±9	O. H.	.78	.55	41 000	58 500	61 400	52 700
15	B	72	934±9	O. H.	.78	.55	20 100	61 500	46 700	39 000
16	B	72	934±9	O. H.	.78	.55	33 900	45 900	43 200	40 000
17	B	72	934±9	O. H.	.78	.55	39 000	66 300	73 400	58 200
18	B	72	934±9	O. H.	.78	.55	15 200	60 600	51 100	38 600
19	B	72	934±9	O. H.	.78	.55	45 600	61 000	57 600	53 500
20	B	72	934±9	O. H.	.78	.55	41 500	52 200	55 500	49 200
21	B	72	934±9	O. H.	.78	.55	33 700	49 200	49 700	43 200
22	B	72	934±9	O. H.	.67	.63	36 400	54 300	53 500	46 800
23	B	72	934±9	O. H.	.67	.63	33 700	57 000	57 000	47 700
24	D	100	1 047±8	Bess	.84	.52	(**C)	(**C)	(**C)	(**C)
25	D	100	1 047±8	Bess	.92	.50	15 800	38 400	23 500	23 400
26	D	100	1 047±8	Bess	.84	.52	28 500	54 000	27 500	33 200
27	D	100	1 047±8	Bess	.84	.52	37 700	43 500	27 000	34 600
28	D	100	1 047±8	Bess	.86	.49	32 200	71 300	21 100	35 600
29	D	100	992±15	O. H.	.64	.65	10 000	24 400	15 000	15 300
30	D	100	992±15	O. H.	.60	.62	12 200	47 900	47 900	33 600

* Not enough ferrite precipitated to permit of a grain count with certainty.

** Too much ferrite in cleavage planes of the crystals which so breaks them up that no count can be made. C Rather coarse; estimated by comparison as approximately 20 000 g. per square inch.

† The C and Mn. percentages were taken from B. S. analyses where available; otherwise from the heat analyses.

[27] The scale of reference is that proposed by Robt. Job. Wm. H. Sellew, Steel Rails, p. 434.

TABLE 23—Continued

Rail No.	Mill	Wt.	Average finishing temperature	Kind	Mn.	C.	Number of grains per square inch			
							Head	Web	Base	Average
		Pounds	° C							
31	D	100	992±15	O. H.	.82	.73	(*)	(*)	(*)	(*C)
32	D	100	992±15	O. H.	.73	.69	(*)	(*)	(*)	(C)
33	D	100	1 047±8	Bess	.76	.44	(**)	32 300	(**)	.....
34	C	90	908±8	O. H.	.72	.70	(*)	(*)	21 500	(C)
35	C	90	908±8	O. H.	.57	.57	17 200	45 000	17 000	22 700
36	C	90	908±8	O. H.	.67	.65	(10 000 est.)	48 900	12 500	18 800
37	C	90	908±8	O. H.	.67	.65	13 800	29 100	18 400	18 700
38	C	90	908±8	O. H.	.67	.65	11 200	25 500	14 100	15 200
39	C	90	908±8	O. H.	.68	.66	(est. ½ W)	43 300	(est. ½ W)	26 600
40	C	90	908±8	O. H.	.67	.65	13 200	22 200	15 500	16 300

* Not enough ferrite precipitated to permit of a grain count with certainty.

** Too much ferrite in cleavage planes of the crystals which so breaks them up that no count can be made.

C Rather coarse: estimated by comparison as approximately 20 000 g. per square inch.

William Campbell has called attention to this point.[28] He states that rails finished, e. g., at 1000° C are not to be classed as coarse-grained material; that reheating rail steel to this same temperature will render it very coarse in comparison.

It would appear probable, then, that the restoration of the crystalline arrangement which is so badly shattered by the squeezing action of the rolls is not so rapid as is generally supposed, and though the restoring process begins immediately after the rolling ceases it is not complete until at a lower temperature, which in fact is the temperature which determines the grain size of the finished product.

Grain Size v. *Amount of Reduction.*—One of the important factors in the determination of the grain size of the rolled piece is the amount of reduction in the rolls. A comparison of the results given in Table 23 shows that for two rails finished at practically the same temperature, the one having the smaller cross section is very much finer grained. The average grain size of the 90-pound and 100-pound rails is 24 000 per square inch, while that of the 72-pound and 75-pound rails is 42 800 per square inch. This is also illustrated by the different parts of the same rail; the web is

[28] Proc. Am. Soc. Test. Materials, 8, p. 353; 1908.

found to have a much finer grain in nearly every case than either the head or base, as is to be expected. The average of the measurements made on 29 rails in which the ferrite network was distinct enough to permit a reliable count gives the following: Head, 26 200 per square inch; web, 44 800 per square inch; base, 36 900 per square inch. These give a practicable working ratio of 2:4:3. The temperature variation throughout the rail and the difference in the rate of cooling in head, web, and base, while exerting some influence upon grain growth, are not great enough to mask or materially alter the effect of the amount of reduction.

Though no definite conclusions can be drawn as to the relative importance of this factor in determining the final structure, since the difference in practice of the various mills, especially in the case of the heavier rails, makes a close comparison impossible; the results are very suggestive, however, and emphasize the importance of further investigation along this line.

Mechanical Properties v. *Grain Size.*—The relation of grain size to mechanical properties is too well determined to require any further support. The results obtained with some of the steels in question are, however, interesting in that they appear as striking exceptions. The following short table (24) is given by Sauveur as typical results showing the variations in mechanical properties with increasing grain size.[29]

TABLE 24

Grains per square inch	Tensile strength per square inch	Elongation of length	Reduction of area
		Per cent	Per cent
44 000	99 000	15	20
54 000	100 000	19	22
104 000	110 000	22.5	35

A comparison of Tables 20 and 23 shows much higher tensile strengths, as well as other mechanical properties with coarser grained steels than is indicated above. The following are a few of the most striking exceptions. Since the tensile specimen was from the head the grain size given is that of the head rather than the mean for the rail.

[29] W. H. Sellew: "Steel rails," p. 424.

TABLE 25

Rail No.	Grains per square inch	Ultimate strength, pounds per square inch	Reduction in area	Elongation in 2 inches
			Per cent	Per cent
9	27 300	111 500	42.8	21.0
18	15 200	106 200	[illegible]	23.5
30	12 200	104 800	27.6	20.0
11	30 700	93 400	51.0	27.5

The results are interesting, however, in emphasizing the fact that the material used for any such comparison must always be strictly defined. Nos. 9, 18, and 30 are of progressively increasing carbon content (0.47, 0.55, and 0.62 per cent) and hence of decreasing percentages of ferrite. This explains, in part at least, the apparent contradiction in properties. No. 11 is low in carbon (0.33) and hence high in ferrite, which accounts for its apparent low tensile strength in spite of the finer grain size. For the accurate determination of the relation between grain size and mechanical properties, it is imperative that the steels compared be of the same composition chemically and differ in no other important respects save in grain size. No such comparison is possible here.

Chemical Composition v. *Microstructure.*—The presence of a high manganese content materially modifies the microstructure of an iron carbon alloy. The general effect of manganese and nickel also is to render the metal slower in its response to any transformation or change, either on heating or cooling.[30] All of the rail steels examined are relatively high in manganese, i. e., they have much more than is actually required to combine with the sulphur present. To this influence of the excess of manganese is to be ascribed the sharp definite boundaries of ferrite surrounding the grains of pearlite. Ordinarily the ferrite coalesces and gathers together while in a semiplastic state during slow cooling under the action of its surface tension, thus obscuring the clear outlines of the network. This action is hindered and partially prevented by the retarding influence of the manganese and this explains why the ferrite net work is clear and definite even after

[30] H. M. Howe: Proc. Am. Soc. Test Materials, 11, p. 365, 1911.

rather slow cooling. The amount of ferrite precipitated also is usually less than is expected from the carbon content.

This is especially true of the open-hearth rails. Due to the higher carbon content of these steels, the influence of the manganese, which is here considerably less than in the Bessemer rails, is great enough to almost entirely prevent the appearance of any ferrite in some cases. The rails thus have the structural appearance of eutectoid steels at low magnification. That the amount of reduction in the rolls bears some relation to the amount of ferrite precipitated seems possible from a comparison of the results obtained with open-hearth rails of different sections (Table 23 and photomicrographs). Though cooled at a slower rate than the rails of smaller section and in some cases finished at a lower temperature (rails 34 to 40) the heavier rails in all cases have a much fainter ferrite network than do the rails of smaller section. This appears to be the case even when the carbon contents of the two sizes are practically the same. (Rails 22–23 *v.* 1–4.) This apparent relation may, however, be only fortuitous. In the Bessemer rails which are lower in carbon, the influence of the manganese is not enough to prevent the precipitation of the ferrite but does hinder its coalescence and makes possible the clear outlines for the grains which are observed. The rate of cooling must be considered in this also. The steel then has the structural appearance, and properties also, of one of higher carbon content. In using the microscopical method for the estimation of carbon in steel, this point merits consideration. This indirect effect of manganese upon the structure of carbon steels is perhaps not as well known by some users of steel as it should be.

Summary.—1. An "effective finishing temperature" somewhat below the observed one is suggested as a possible explanation why rails finished, e. g., at 900°–1000° are not as coarse grained as might be expected.

2. So far as can be judged from the data in hand the amount of reduction of section in the rolls appears to be as effective in determining the grain size as any other factor.

3. For the determination of any numerical relation between mechanical properties and grain size a study of the same kind of steel under varying conditions is essential.

4. The effect of manganese in retarding the condition of equilibrium during cooling is an important one upon the structure and properties of rail steel of composition similar to the 40 rails studied.

Representative photomicrographs illustrating the microstructure typical of the different conditions are given in Figs. 12, 13, 14, and 15, at the close of the paper.

11. TEMPERATURE DISTRIBUTION IN A COOLING RAIL

In order to determine how much the readings of the optical pyrometer differ from the true temperatures of the inner metallic surface and center of railhead, measurements were made in the laboratory on the cooling of a 24-pound length of a 100-pound rail section (for analysis, see R. 30 of Table 17) 8½ inches long, which was heated in a muffle to a uniform temperature throughout of about 1070° C, then removed from muffle and allowed to cool in the air, resting on its base.

As shown in Fig. 6 for one of three series, measurements of the temperature of the center of head (A) and inner surface (B) were taken with thermocouples and the head was also sighted upon at B with the same optical pyrometer used in the mills. (See sec. 5.) The three time-temperature cooling curves obtained (1) with thermocouple at center of head A, indicated by + + +; (2) with another couple at surface B, indicated by × × ×; and (B) with optical pyrometer, indicated by ⊙ ⊙ ⊙; all show the critical range very markedly, and even the optical pyrometer detects the recalescence or rise in temperature accompanying the reaction.

It will be seen that, after cooling has set in, the center of the head remains about 40° C (100° F) to 30° C hotter than the inner surface until the critical range is approached, when the rail takes on a nearly uniform temperature throughout. The readings of the optical pyrometer are about 40° C lower than the inner surface temperature at 1000° C (1830° F) and 80° C lower than the center of the head, but all three become practically identical from 800° C (1470° F).

In Table 26 are given the relations between these various temperatures for the three series taken. The observations with the optical pyrometer were made by a different observer for each

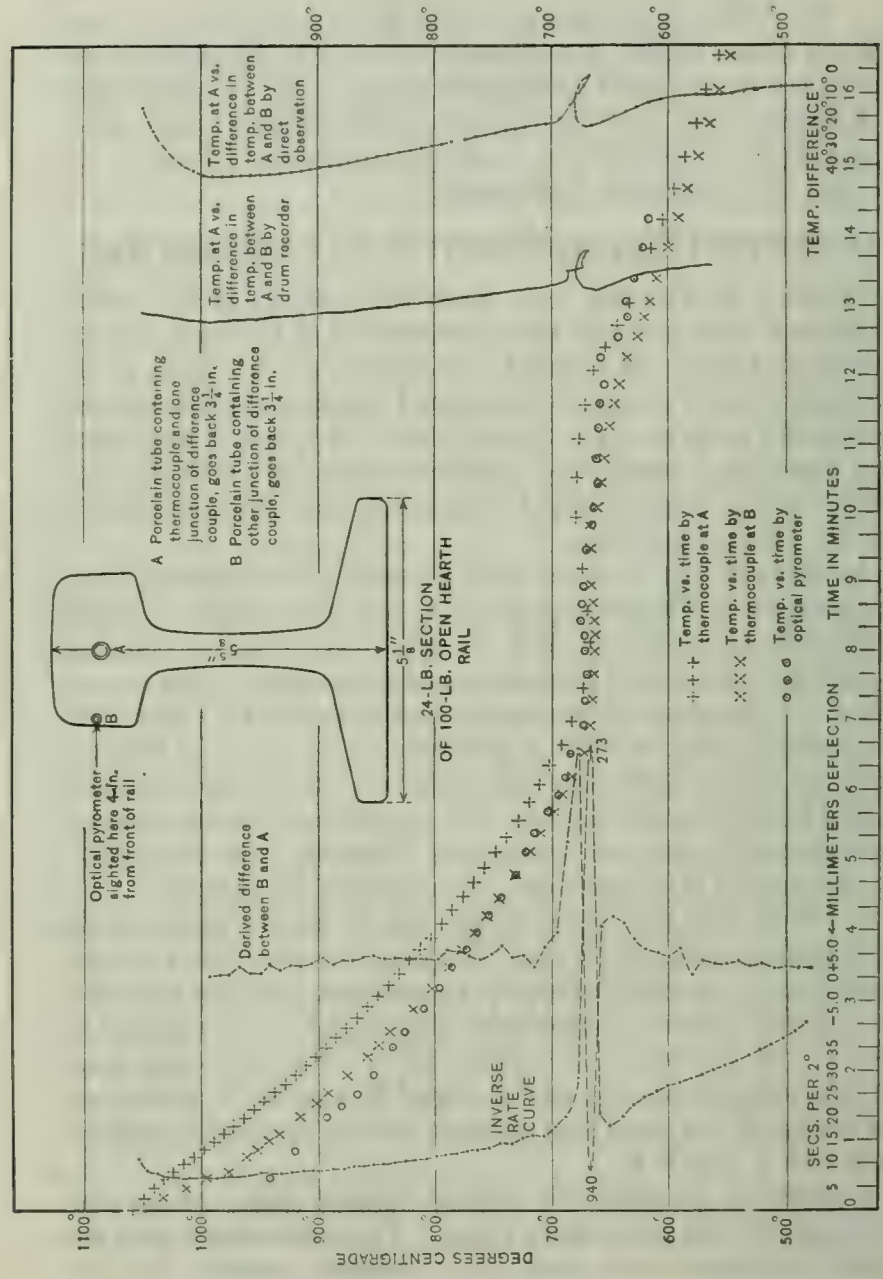

DEGREES CENTIGRADE
1100°
1000°
900°
800°
700°
600°
500°
900°
800°
700°
600°
500°
Temp. at A vs. difference in temp. between A and B by direct observation
Temp. at A vs. difference in temp. between A and B by drum recorder
A Porcelain tube containing thermocouple and one junction of difference couple, goes back 3¼ in.
B Porcelain tube containing other junction of difference couple, goes back 3¼ in.
5⅛"
24-LB. SECTION OF 100-LB. OPEN HEARTH RAIL
Optical pyrometer sighted here 4 in. from front of rail
Derived difference between B and A
INVERSE RATE CURVE
940
273
Temp. vs. time by thermocouple at A
Temp. vs. time by thermocouple at B
Temp. vs. time by optical pyrometer
SECS. PER 2°
5 10 15 20 25 30 35 −5.0 0 +5.0 ← MILLIMETERS DEFLECTION
TIME IN MINUTES
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
TEMP. DIFFERENCE
40° 30° 20° 10° 0

Fig. 6.— *Cooling of 100-pound rail section*

series. It is evident that the three series are in substantial agreement. The average time for the rail to cool from 1070° C to the beginning of the critical range, 670° C, was 8 minutes 30 seconds.

In Fig. 6 are also shown other types of cooling curves taken simultaneously with the above, namely, the inverse rate curve taken with the thermocouple at A; the derived difference curve taken with the thermocouple at A, and a differential thermocouple, the junctions of which are at A and B, respectively; and two difference curves, one giving the temperature of A in terms of the difference in temperature between A and B by direct observations of the thermocouple readings, and the other giving the same phenomenon taken with a Leeds and Northrup drum recorder connected in parallel with the observing circuits. The cooperation of five observers was required to obtain the data for all the plotted curves.

TABLE 26

Temperature Distribution in 100-pound Rail Cooling from 1070° C

Time intervals	With thermocouples		With optical pyrometer outer surface at B	Average differences	
	Center of head at A in fig. 6	Inner surface at B in fig. 6		(2)–(3)	(2)–(4)
(1)	(2)	(3)	(4)	(5)	(6)
Secs.	°C	°C	°C	°C	°C
40	1050	1040	...	15	70
38		1035	...		
(a)	....	...	...		
40	1000	955	920	40	85
41		970	915		
36		950	910		
42	950	905	885	[illegible]	70
[illegible]		920	885		
38		905	870		
51	900	860	845	35	55
51		870	850		
43		865	845		
56	850	810	805	30	40
56		825	810		
50		820	805		
64	800	765	765	25	30
66		780	775		
57		775	770		

[a] Third series from a temperature less than 1070° C.

TABLE 26—Continued

Time intervals	With thermocouples		With optical pyrometer outer surface at B	Average differences	
	Center of head at A in fig. 6	Inner surface at B in fig. 6		(2)-(3)	(2)-(4)
(1)	(2)	(3)	(4)	(5)	(6)
Secs.	°C	°C	°C	°C	°C
80	750	720	720	20	20
80		730	730		
70		735	735		
75	700	675	685	15	10
67		685	690		
66		685	700		
288	670	665	670	5	0
295		665	675		
258		665	...		
	650	630	640	10	0
		635	660		
		655	...		

12. EXPANSION OF RAIL STEELS

The determinations of the expansion of rail steels were made on strips 50 by 0.95 by 0.65 cm, cut from representative steel rails from the several rail mills. The expansion apparatus was kindly loaned by Dr. A. L. Day, director of the Geophysical Laboratory, Carnegie Institution of Washington.

The bars were cut from the flange of the rails, and as the rail lengths at our disposal were less than 50 cm it was necessary to weld two pieces to obtain a specimen for expansion. Platinum inserts were put in the ends of the specimens and 0.5 mm divisions were marked with a dividing engine. The telescopes, fitted with micrometer screws, were sighted on these divisions. All the bars were heated in an oxidizing atmosphere (air), no attempt being made to close the small openings through which the telescopes were sighted. The bars oxidized slowly, but hardly enough to influence their expansion. Bar 7–11 was packed in steel filings inclosed in a marquardt tube. The filings oxidized and expanded, binding the bar. This probably accounts for the

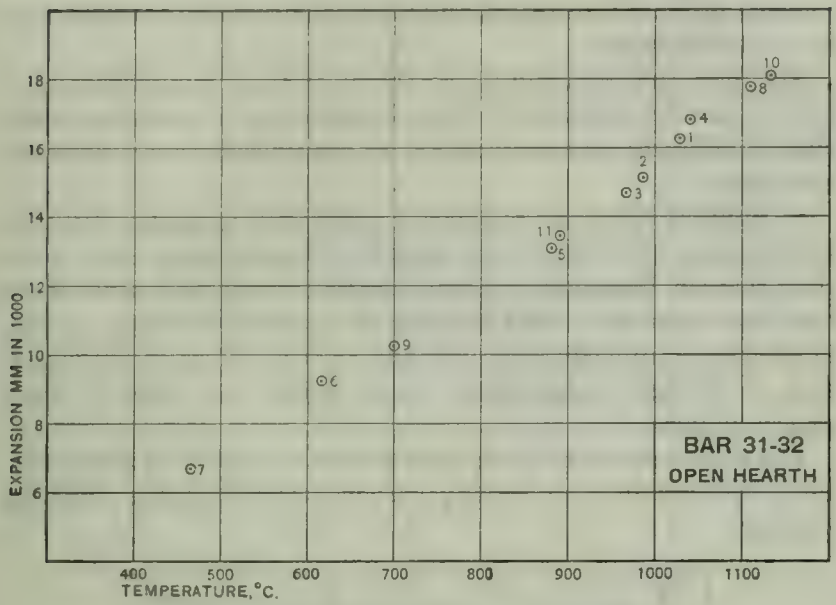


Fig. 7.—*Expansion observations of open-hearth steel*

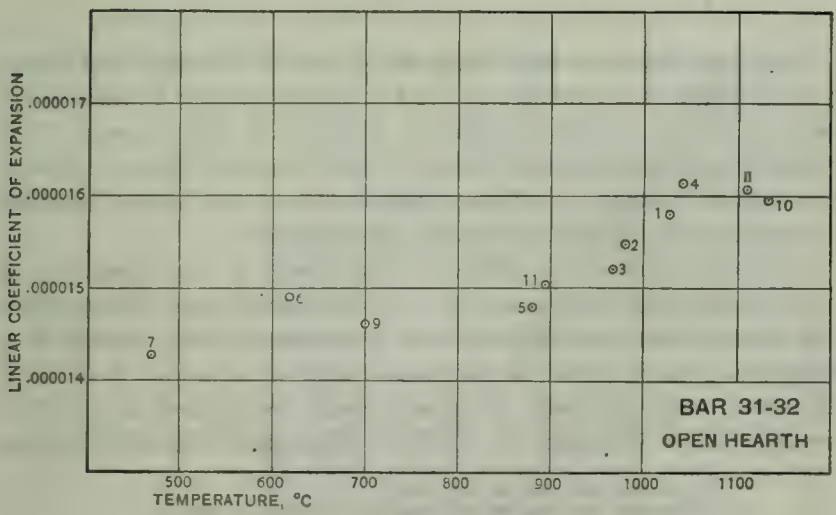


Fig. 8.—*Expansion coefficient of open-hearth steel*

unusual increase in length found for this bar at room temperature after each heating.

The data and results given in Tables 27 to 30 and in Figs. 7, 8, and 9 show determinations of the expansion and expansion coefficient at different temperatures for an open-hearth and a Bessemer specimen.

It appears that the expansion coefficient increases with the temperature, the increase for open-hearth steel being much more than that for Bessemer. It was also found that with some of the bars the expansion would increase on repeated heatings, so that in showing graphically, Figs. 10 and 11, the values of the expansion at different temperatures more weight was given to early determinations.

The dotted curves of these figures show the results of determinations by Driesen [32] on cooling carbon steels with the following analyses:

Fig.	C	Mn	Si	P	S	Cu
10	0.81	0.10	0.06	Tr.	0.025	0.02
11	0.56	0.09	0.04	Tr.	0.023	0.02

He found, as have other observers,[33] that on heating steel above 700° C there is a contraction, and a corresponding expansion on cooling. This feature is plainly marked in the curves. Our results would indicate this break in the expansion, but as we were interested primarily in higher temperatures, the exact location and extent of this change was not investigated.

Quite an appreciable difference was found in the expansion of open-hearth and Bessemer rails. An open-hearth rail, of the chemical composition here given, with a shrinkage after rolling of 6 inches in 33 feet would be finished at 975° C, or 1790° F, while a Bessemer with the same shrinkage would be finished at 1030° C, or 1890° F, a difference of 100° F. This great difference in the

[32] Joh. Driesen, Ferrum, 5, p. 17; 1914.
[33] Svedelius, Phil. Mag., **96**, 1898; Charpy and Grenet, C. R., **134**, 1902.

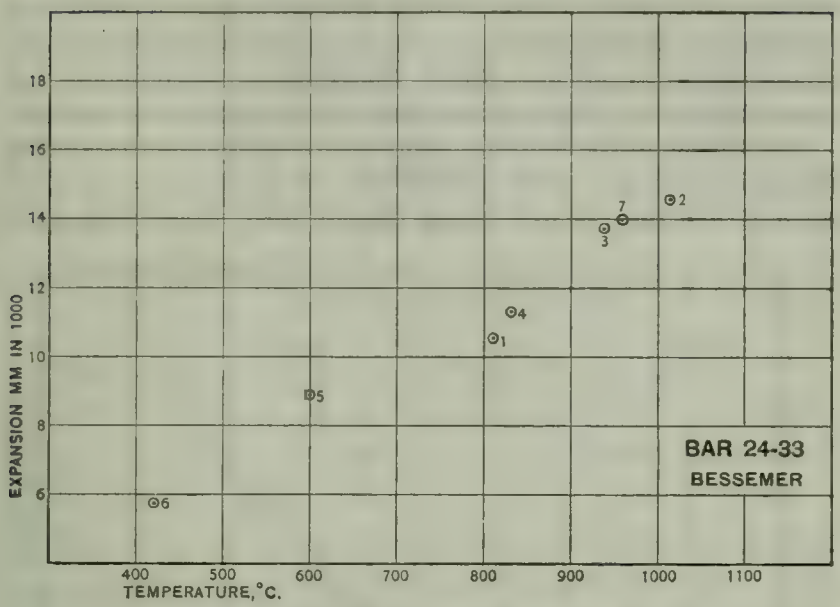


Fig. 9.—*Expansion observations of Bessemer steel*

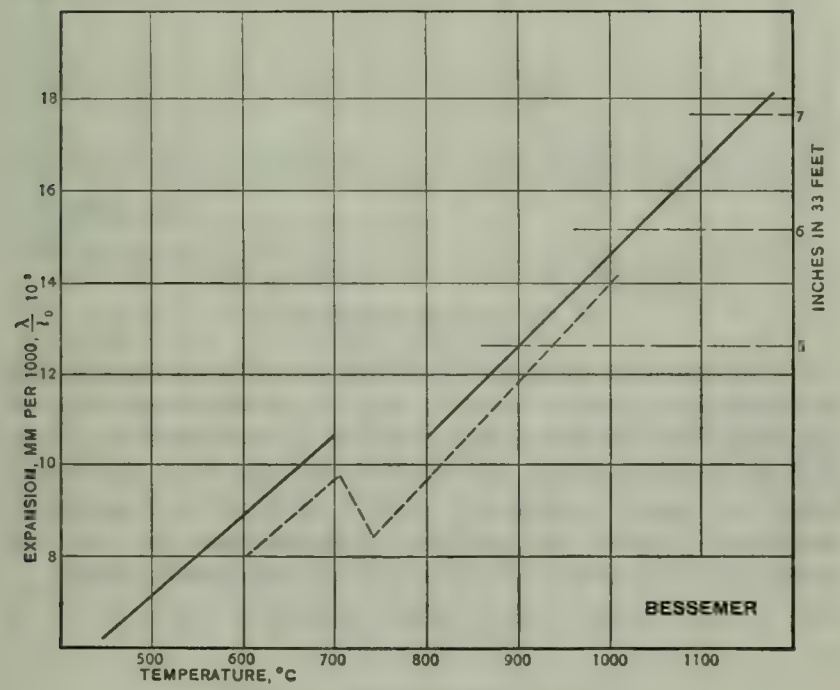


Fig. 10.—*Expansion of Bessemer steel*

shrinkage of the two classes of rails does not appear to have been considered in rail specifications, although this difference must have been detected in mill practice.[34] This difference is probably still greater for the very high carbon open-hearth rails now so common.

Any change in the finishing temperature makes a corresponding change in the length of the finished rail. If the hot saws are set to cut a 33-foot open-hearth rail at 1800° F, 980° C, a shrinkage of

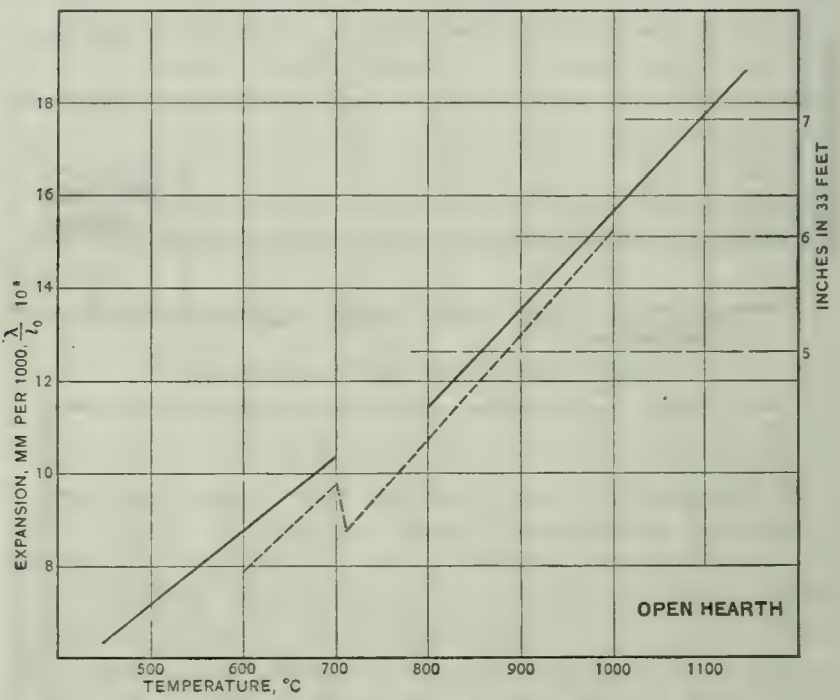


Fig. 11.—*Expansion of open-hearth steel*

$6\frac{1}{16}$ inches must be allowed. If another rail with the same setting of the hot saws is cut at 1900° F, 1040° C, the shrinkage would be $6\frac{9}{16}$ inches, and the final length would be ½ inch less than 33 feet. Rail specifications usually allow ¼ inch variation from the desired length, so that a variation of 100° F in finishing temperature appears to be more than sufficient to differentiate the rails that would pass from those that would not pass the specifications.

[34] See, for example, S. S. Martin, Rail rolling at lower temperatures in 1901. Iron Age, 68, p. 4; sec. 26; 1901.

In Figs. 10 and 11 are given the expansions in millimeters per 1000 mm for the Bessemer and open-hearth rails, respectively. The mean expansion coefficient for any temperature (C) may be obtained[35] by dividing the expansion by that temperature × 1000.

TABLE 27

Bar 24–33

[Bessemer rails; bars electrically welded. Analysis: C, 0.50; S, 0.042; P, 0.081; Mn, 0.93; Si, 0.101; Cu, 0.007; Ni, 0.06; Cr, 0.00]

Date	Length—		Temperature t° C	Expansion	
	At 20° C	At t° C		In 500 mm 0–t	Coefficient
	Mm	Mm		Mm	
November 25, 1913....	500. 25				
Do.....		505. 08	810	5. 29	. 00001305
Do.....	499. 96				
November 28, 1913....	499. 90				
Do.....		506. 73	1014	7. 25	1429
November 29, 1913....	499. 70				
Do.....		505. 79	936	6. 87	1469
December 1, 1913.....	499. 12				
Do.....		504. 31	830	5. 67	1367
Do.....		303. 08	600	4. 42	1473
Do.....		501. 58	423	2. 90	1371
December 2, 1913.....	498. 81				
Do.....		505. 59	[illegible]	6. 99	1444

[35] Sample computation of expansion (see formula, sec. 4): Take from Table 29, rail bar 31–32, the observation at 1028° C. Assume the coefficient of expansion between 0° and 20° the same for all rails, or $\alpha^{20}_{0}=0.000011$.

Expansion from 20° to 1028°: 507.17−499.29=7.88 mm.

Length at 20° C=l_{20}=500−7.88=492.12 mm.

Length at 0° C=$l_0=\frac{492.12}{1+0.000011\times 20}=492.01$ mm.

Expansion 0° to 1028° C=500−492.01=7.99 mm.

Mean coefficient between 0° and 1028° C: $\alpha^{t}_{0}=\frac{7.99}{492.01\times 1028}=0.00001580$

Expansion: mm in 500 between 0° and 1028° C: 0.00001580×500×1028=8.11 mm.

TABLE 28

Bar 7–11

[Bessemer rails; bars threaded together and welded with oxyacetylene. Analysis: C, 0.39; S, 0.071; P, 0.067; Mn, 0.90; Si, 0.035; Cu, 0.105; Ni, 0.12; Cr, 0.17]

Date	Length—		Temperature t° C	Expansion	
	At 20° C	At t° C		In 500 mm 0–t	Coefficient
	Mm	Mm		Mm	
January 23, 1914	499.98				
Do		507.18	1051	7.42	.00001412
Do		506.39	919	6.61	1438
Do		506.20	855	6.41	1500
January 24, 1914	501.37				
Do		508.28	1040	7.12	1369
January 26, 1914	501.65				

TABLE 29

Bar 31–32

[Open-hearth rails; bars threaded together and welded with oxyacetylene. Analysis: C, 0.66; S, 0.033; P, 0.028; Mn, 0.66; Si, 0.160; Cu, 0.016; Ni, 0.00; Cr, 0.01]

Date	Length—		Temperature t° C	Expansion	
	At 20° C	At t° C		In 500 mm 0–t°	Coefficient
	Mm	Mm		Mm	
February 18, 1914	499.97				
Do		507.17	1028	8.13	.00001580
Do		506.65	980	7.59	1548
Do		506.43	968	7.36	1520
February 20, 1914	499.29				
Do		506.92	1042	8.41	1614
Do		505.09	880	6.51	1480
Do		503.21	617	4.60	1492
Do		501.98	470	3.35	1427
Do		507.42	1110	8.92	1608
February 21, 1914	498.76				
February 24, 1914	498.68	503.64	701	5.12	1461
Do		507.02	1132	9.03	1595
Do		504.78	894	6.72	1503
February 25, 1914	498.26				

TABLE 30

Bar 34–39

[Open-hearth rails; bars threaded together and electrically welded. Analysis: C, 0.70; S, 0.057; P, 0.025; Mn, 0.72; Si, 0.079; Cu, 0.026; Ni, 0.00; Cr, 0.01]

Date	Length—		Temperature t° C	Expansion	
	At 20° C	At t° C		In 500 mm 0–t° C	Coefficient
	Mm	Mm		Mm	
January 9, 1914	499.95				
Do		507.37	1040	8.31	.00001599
January 10, 1914	499.30				
January 12, 1914		508.11	1036	9.10	1757
Do		507.45	904	8.42	1863
January 13, 1914	499.28				
Do		508.11	1021	9.43	1848
Do		507.15	884	8.44	1857
January 15, 1914	498.96				
Do		503.43	621	4.54	1462
January 16, 1914	499.04				
Do		503.30	625	4.41	1411
Do		502.06	462	3.15	1364
Do		509.19	1022	10.34	2023
January 17, 1914	499.17				

Shrinkage Measurements.—In addition to the measurements on the expansion of the 50 cm specimens of rails, one series of shrinkage observations was taken in mill B on 75 open-hearth 100-pound G section rails. (See Table 31.) The rails had the following heat analysis: C=0.710; Mn=0.90; P=0.025; S=0.045; Si=0.100.

First, the distance between the hot saw and stop was carefully measured with a steel tape, then as the rails were stopped under the hot saw the temperatures were measured and a note made of the thickness of the paddle used against the stop. The rails were marked and left on the cooling beds over night and the length of each measured cold.

From the observations thus obtained the coefficient of shrinkage was found to be 0.0000161,[35a] which is in good agreement with the

[35a] Computation of shrinkage coefficient:

Temperature of rails as measured with pyrometer, 947° C.
Temperature of rails corrected by Table 26, 997°.
Shrinkage of rails, measured at 25° C, 6.24 inches.
Shrinkage of rails, corrected to 0° C, 6.35 inches.
Length of rails, 396 inches.

$$a=\frac{6.35}{997\times 396}$$

$a=0.0000161$

results obtained on the shorter lengths for the expansion coefficient of open-hearth rails, namely, $\alpha = 0.0000156$.

TABLE 31.—Shrinkage Measurements on Open-Hearth 100-Pound G Section Rails

Mean ABCDEF=947° C.=0.520 feet=6.24 inches

A rail		B rail		C rail		D rail		E rail		F rail	
Temperature	Shrinkage	Temperature	Shrinkage	Temperature	Shrinkage	Temperature	Shrinkage	Temperature	Shrinkage	Temperature	Shrinkage
° C	Feet	° C	Feet	° C	Feet	° C	Feet	° C	Feet	° C	Feet
974	0.530	951	0.517	945	0.509	970	0.541	949	0.518	939	0.509
950	.528	930	.520	.....	.....	968	.530	948	.505	.....	.....
945	.529	934	.518	936	.509	945	.528	928	.519	.....	.....
959	.540	954	.519	945	.504	965	.535	958	.520	948	.510
939	.520	943	.500	930	.514	959	.530	956	.510	944	.509
951	.530	943	.505	.....	.....	968	.530	958	.530	.....	.....
975	.530	965	.520	.....	.....	960	.520	943	.502	.....	.....
954	.530	951	.505	951	.501	945	.530	945	.520	935	.511
958	.530	957	.515	946	.507	949	.535	956	.515	939	.514
928	.525	934	.520	928	.519	936	.520	943	.515	934	.528
951	.541	943	.510	930	.500	951	.525	923	.510	.....	.....
958	.540	943	.510	936	.529	945	.510	926	.514	.....	.....
961	.540	956	.522	950	.514	948	.532	945	.528	939	.517
953	.540	956	.525	945	.524	953	.530	946	.510	934	.511
Mn 954	.532	947	.515	940	.512	954	.528	945	.515	939	.515

13. "SHRINKAGE CLAUSE" IN RAIL SPECIFICATIONS

It may be of some interest to recall certain salient features in the history of the "shrinkage clause" in American rail specifications. We shall pay particular attention to those of the A. S. T. M. and A. R. E. A. as typical.

Mr. Cushing, in his instructive account of the improvement of rail design and specifications from 1893 to the present time,[36] states that:

> In view of the agitation for colder rolling, the Pennsylvania Railroad had introduced into its specifications in 1900 a clause requiring that the rail at the last pass should be at a red heat, preferably a dull red, but in 1901 they replaced it with a so-called "Shrinkage clause," which was intended to control the temperature of the rail when being finished, by prescribing that the shrinkage, after the rail was sawed, should not exceed a certain number of inches. This clause was also introduced into

[36] W. C. Cushing; A. R. E. A. Bull., 13, p. 853, 1912.

the proposed specifications of the engineering association, making an additional requirement for the details of manufacture.

The rail specifications adopted in 1901 by the A. S. T. M. contained no shrinkage clause. The A. Ry. A. and A. Ry. E. & M. W. A. proposed such a clause in 1902 and in 1904 adopted the following:

The number of passes and speed of train shall be so regulated that on leaving the rolls at the final pass the temperature of the rail will not exceed that which requires a shrinkage allowance at the hot saws of 6 inches (in 33 feet) for 85-pound and $6\frac{1}{8}$ inches for 100-pound rails, and no artificial means of cooling the rails shall be used between the finishing pass and the hot saws. The above shrinkage allowance may be varied, if necessary, so as to give a finishing temperature of not exceeding 1600° F at finishing rolls for mills rolling from reheated blooms and not exceeding 1750° F at finishing rolls for mills rolling direct from the bloom to finished rail.

A shrinkage of $6\frac{1}{8}$ inches in 33 feet is equivalent to a finishing temperature of about 1815° F (990° C) for open-hearth rails and of 1913° F (1045° C) for Bessemer rails, according to the expansion measurements of section 12.

The adoption of a shrinkage clause was discussed annually from 1901 by the A. S. T. M., but without action until 1907. In 1906 the iron and steel committee of the A. S. T. M. recommended the adoption of a shrinkage allowance of $6\frac{11}{16}$ inches in 30 feet ($7\frac{11}{32}$ inches in 33 feet), equivalent to 2075° F for open-hearth or 2190° F for Bessemer rails, as compared with the $6\frac{1}{8}$ inches in 33 feet of the A. R. E. A., or advocating a finishing temperature of over 250° F higher than the A. R. E. A. specifications allowed.

In 1907 the A. S. T. M. adopted the following shrinkage clause:

The number of passes and speed of train shall be so regulated that on leaving the rolls at the final pass the temperature of the rail will not exceed that which requires a shrinkage allowance at the hot saws, for a 33-foot rail of 100-pound section, of $7\frac{5}{16}$ inches and $\frac{1}{16}$ inch less for each 5 pounds decrease in section. These allowances to be decreased at the rate of 0.01 inch for each second of time elapsed between the rail leaving the finishing rolls and being sawn. No artificial means of cooling the rails shall be used between the finishing pass and the hot saws.

This was practically equivalent to the committee recommendation of the preceding year and in effect permitted finishing Bessemer rails at 2187° F (1197° C) or at 940° F (505° C) above the recalescence region of rail steel.

The A. S. T. M. in 1909 reduced this shrinkage allowance on 100-pound sections to $6\frac{3}{4}$ inches in 33 feet, or to an equivalent of 1947° F (1064° C) for open-hearth and 2055° F (1124° C)

for Bessemer rails. This specification, which also does not contain the time restriction from last pass to hot saws, is still in force (1914) and reads as follows (see 1913 Year Book, A. S. T. M.):

The number of passes and speed of train shall be so regulated that on leaving the rolls at the final pass the temperature of rails of sections 75 pounds per yard and heavier will not exceed that which requires a shrinkage allowance at the hot saws of $6\frac{7}{16}$ inches for a 33-foot 75-pound rail, with an increase of $\frac{1}{16}$ inch for each increase of 5 pounds in the weight of section.

The shrinkage allowed by the specifications of the A. Ry. A. and A. R. E. & M. W. A. has been in general less than for those of the A. S. T. M. (See Bull. A. Ry. A., p. 254, 1910.)

In 1910 the former associations had the following shrinkage clause "intended as a guide in the preparation of future specifications":

Shrinkage: 5. The number of passes and speed of train shall be so regulated that, on leaving the rolls at the final pass, the temperature of the rails will not exceed that which requires a shrinkage allowance at the hot saws, for a 33-foot rail of 100 pounds section, of $6\frac{1}{2}$ inches for thick base sections and $6\frac{3}{4}$ inches for A. S. C. E. sections, and $\frac{1}{8}$ inch less for each 10 pounds decrease of section, these allowances to be decreased at the rate of $\frac{1}{100}$ inch for each second of time elapsed between the rail leaving the finishing rolls and being sawed.

This is equivalent to a maximum finishing temperature of 1895° F (1035° C) for thick base open-hearth rails of 100-pound section.

The American Society of Civil Engineers allow only $6\frac{7}{16}$ inches for 100-pound sections, or the equivalent of a maximum finishing temperature of 1880° F (1027° C) for open-hearth rails.

The Association of American Steel Manufacturers have no temperature clause in their specifications for rails and those of the United States Steel Products Co. state that "a uniform finishing temperature (must be) also maintained."

The practice of the rail mills regarding the actual shrinkage used as given by Sellew [37] in 1913 shows a minimum shrinkage allowance for rails of 100-pound section of $5\frac{5}{8}$ inches (1705° F for open hearth) and a maximum of $6\frac{3}{4}$ inches (1947° F for open hearth), most of the mills using a shrinkage of $6\frac{5}{8}$ inches or over, corresponding to finishing temperatures of 1920° F or over for open-hearth rails.

[37] W. H. Sellew: "Steel rails," p. 444, Van Ostrand Co., Pub., 1913.

As shown in section 5, and as would be expected from the nature of the process of rolling, starting with blooms of a given weight and section, the rails of heavy section are generally finished at a higher temperature than those of light section, although this is not the practice for all mills. This is recognized in most specifications by allowing a shrinkage of "one-eighth inch less for each 10 pounds decrease in section" (from, say, the 100-pound section). This clause is equivalent to finishing 80-pound rails at 50° F lower temperatures than 100-pound rails.[38]

If it be considered desirable to finish rails of all sections at the same temperature, this could readily be accomplished in practice by starting with ingots (in a continuous mill) or with blooms (in a mill with reheated blooms), the temperatures of which have been adjusted (see also sec. 3) before rolling into rails. On the whole, it would seem to be better practice, if the best possible product is desired, to finish the rails of heavy section at a lower temperature than those of lighter sections. It should perhaps be again emphasized at this point that it is not difficult to control pyrometrically rolling temperatures.

To recapitulate concerning the shrinkage clause, it is apparent that an intelligent effort was made about 1901 to limit excessive rolling temperatures by endeavoring to define the maximum finishing temperature at about 1600° to 1750° F, but the methods of measuring temperatures then in vogue did not permit a suitable pyrometric control, so that recourse was had to the shrinkage of the rail at the hot saw to define the finishing temperature, although no account was then or has been since taken of the different contraction for various steels.

It would seem, moreover, that the value then generally assigned to the shrinkage (say from 1904) did not give an exact idea of the finishing temperature, and this shrinkage allowance, as finally adopted, is unduly high, due in part to pressure from the manufacturers. It will also be recalled that the present rolling practice in four representative mills (sec. 9, Table 3) is on the average some 500° F or more above the recalescence region, but well within the shrinkage specifications.

[38] For example, see A. R. E. A. specifications of November, 1912, in Bull. A. R. E. A., 14, p. 185, 1912; also A. S. T. M. 1913 year book, p. 325.

The maximum finishing temperature allowed by the A. S. T. M., 2055° F (1124° C), is above the temperature of rolling of many ingots for rails, as shown by the measurements in section 5.

From an examination of the voluminous literature on the subject of finishing temperatures as influencing properties of rails, one readily gathers the consensus of opinion to the effect that rails should not be finished too high above their critical region. Nevertheless they are actually finished at very much higher temperatures, and this under a clause in specifications originally drawn with the purpose to limit the maximum allowable finishing temperature to slightly above the critical range.

It would appear therefore that the present "shrinkage clause" of such specifications as those of the A. S. T. M., for example, has no significance whatever.

14. SUMMARY AND CONCLUSIONS

The main objects of this investigation were to determine, from measurements taken in representative rail mills, the present American practice regarding the temperatures at which rails are rolled, to demonstrate the ease and accuracy with which such temperatures may be measured, to find out what the "shrinkage clause" in rail specifications really means, and finally to determine for rail steels some of the physical properties, particularly those of interest in manufacture and some of which, it would seem, are not sufficiently well known as yet. Among these last are the expansion, melting ranges, critical ranges, and temperature distribution throughout a rail section on cooling.

Among the results obtained from measurements in four mills are: Ingots for rails are rolled at temperatures ranging from 1075 to 1150° C (1965 to 2100° F), and the variation from one ingot to another in a series of 20 to 40 is only 10 to 20° C. (See Table 15.)

Rails are finished at temperatures ranging from 880° C (1615° F) to 1050° C (1922° F), but usually ranging within 50° C of 935° C (1715° F). (See Table 16.)

The finishing temperature of each rail may be measured at the hot saws. (See Tables 4 to 14.)

With uniform mill practice, the rails of 100-pound section will be finished at some 10 to 20° C hotter than 90-pound rails and about 50° C hotter than 75-pound rails. (See Table 16.)

It is possible to roll rails, all of which, of a given position in the ingot as A or B, etc., will be finished within ±10° C of the same temperature. (See Table 8.)

Chemical analyses and metallographic examinations were also made and the mechanical properties determined for a number of samples of rail the rolling of which had been observed. From a comparison of these not very numerous observations, there does not appear to be a sufficient degree of correlation to warrant associating very specifically any of the characteristics defined by these three methods of examination, either with the temperatures of rolling here observed or with each other. (See secs. 7, 9, 10, for details.)

The following thermal properties of these rail steels were determined in the laboratory:

The critical range on heating is located (maximum) to within 7° C of 732° C (1350° F) for the 10 samples of open hearth and Bessemer steels examined. On cooling, the critical range lies between the limits 680° C (1256° F) and 650° C (1202° F).

The melting or freezing range for rail steel extends from about 1470° C (2680° F) to nearly the melting point of iron, located at 1530° C (2786° F).

The expansion for open hearth and Bessemer steel is not the same. Above 800° C (1470° F) the expansion for both increases linearly with temperature and the linear coefficient per degree centigrade has the following mean values between 0° and 1000° C:

For Bessemer steel (carbon 0.40 to 0.50 per cent): $\alpha = 0.0000146$.
For open-hearth steel (carbon 0.65 to 0.70 per cent): $\alpha = 0.0000156$.
From shrinkage measurements taken in the rolling mill, open-hearth steel (C = 0.71) has a coefficient between 0° and 1000° C of ..... $\alpha = 0.0000161$.

A rail of 100-pound section cooling freely in air from a uniform temperature of 1070° C (1960° F) reaches its recalescence point at 670° C (1238° F) in about 8 minutes 30 seconds. The maximum difference in temperature between center and outside of head

during this cooling is about 85° C at 1000° C (1832° F), becoming 0° again at 670° C.

A comparison of the shrinkage clause in American rail specifications (for example that of the A. S. T. M.) with the expansion of rail steel shows that this clause permits finishing rails at 1120° C (2045° F) or 450° C (842° F) above the critical range of rail steel, and above the temperature at which many ingots for rails are actually rolled in practice. Such a shrinkage clause therefore does not serve the avowed purpose of limiting the finishing temperatures to a value slightly above the critical range.

In conclusion, it should be emphasized that the various series of observations recorded in this investigation are of but a preliminary nature and do not pretend to solve the question of the relations between temperature of rolling and the properties of rails. It would seem desirable, as herein suggested, to make a much more complete and comprehensive study of the various matters mentioned and of related questions than has hitherto been attempted, and on a scale commensurate with the importance to the community of the problem of sound rails.

The authors regret it is impossible to mention by name the several rail mills at which observations were taken, but nevertheless take this opportunity of expressing their appreciation of the facilities accorded them and are glad to acknowledge that all the four companies concerned have offered the further use of their plants for similar investigations.

Finally, it is with great pleasure that acknowledgment is made of the willing and efficient assistance rendered by H. Scott in taking and reducing observations, and also of help from members of the chemical, heat, engineering, and weights and measures divisions of the bureau.

WASHINGTON, April 28, 1914.

EXPLANATION OF FIGS. 12, 13, 14, AND 15

All photomicrographs are taken at a magnification of 100× after etching with picric acid. The samples were taken as illustrated in Fig. 5, unless stated otherwise. All represent vertical longitudinal sections.

Fig. 12, A–F, and Fig. 13, A–B, represents a medial longitudinal section of rail No. 8, a 75-pound Bessemer rail.

A=upper surface of the rail. The metal has been somewhat decarburized on the surface.

B–F (and A–B, Fig. 13). A series of samples taken about 1.5 cm apart in a medial longitudinal section beginning with the head. (Height of rail, 12 cm.) The variation in grain size may be taken as typical of rails of this kind and weight.

Fig. 13, C–F=rail No. 3, a 100-pound open-hearth rail.

C=upper surface. The outer skin has been somewhat decarburized.

D–E–F=head, web, and base, respectively.

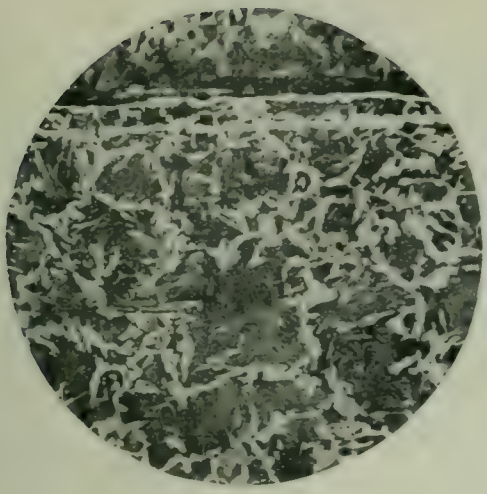
The figure illustrates the fact that microscopic examination of the surface only may give an erroneous idea of the true structure of the interior.

Fig. 14, A–B–C=head, web, and base, respectively, of rail No. 11, a 75-pound Bessemer rail. Though low in carbon (0.33) the structure is that of a steel considerably higher. The retarding effect of manganese and nickel in delaying the coalescence of the ferrite is well illustrated here.

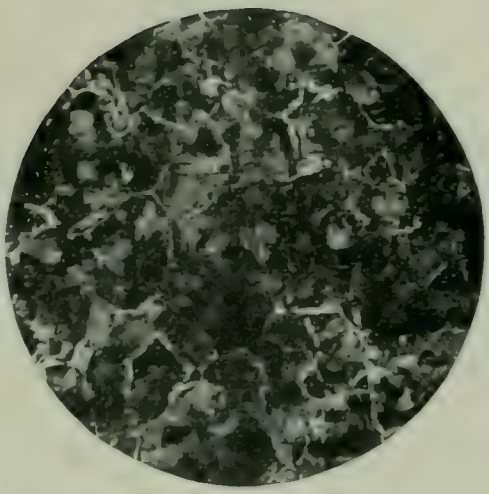
D–E–F=head, web, and base, respectively, of rail No. 18, a 72-pound Bessemer rail. The structure and grain size are typical of the small-section Bessemer rails examined.

Fig. 15, A–B–C=head, web, and base, respectively, of rail No. 25, a 100-pound Bessemer rail. Though one of the coarsest of the Bessemer rails observed, its physical properties compare very favorably with the others.

D–E–F=head, web, and base, respectively, of rail No. 32, a 100-pound open-hearth rail. The rail is typical of the large-section open-hearth rails, and shows an apparent carbon content considerably in excess of the real.



A



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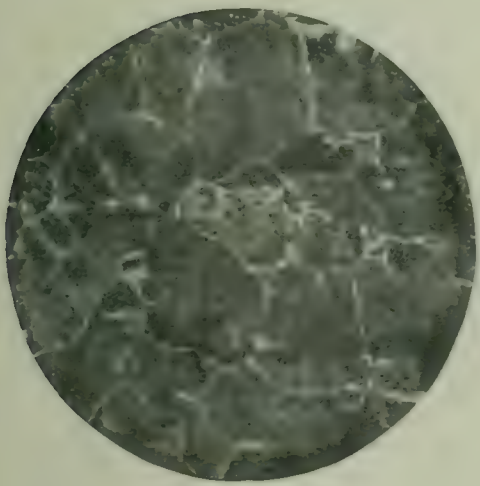
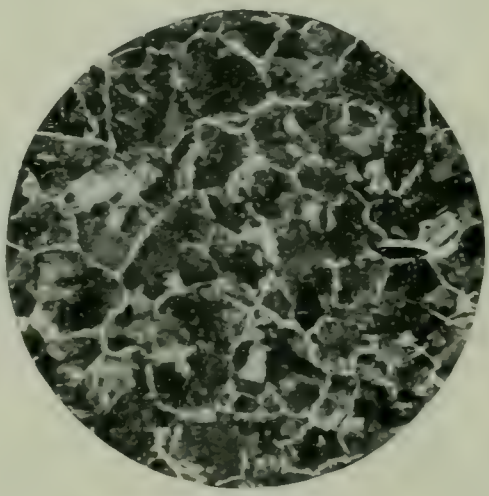
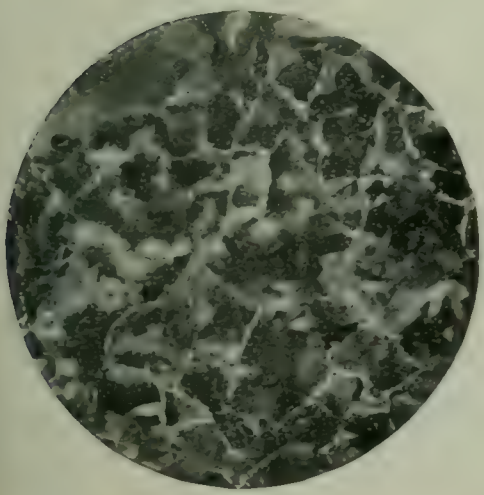


B



E



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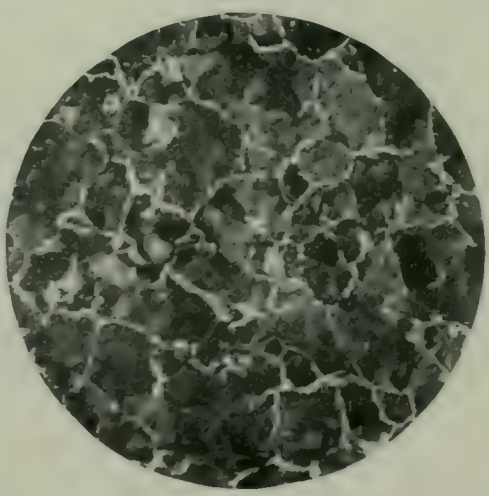

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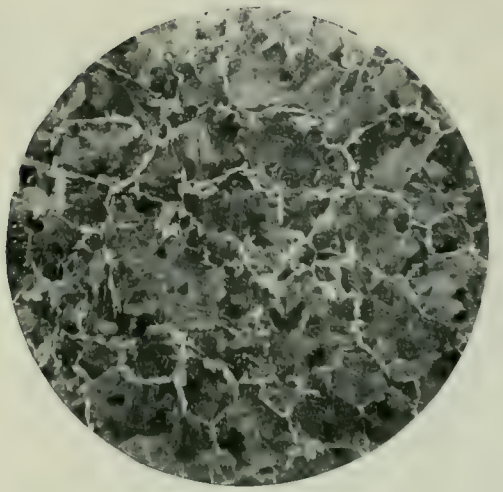
Fig. 12



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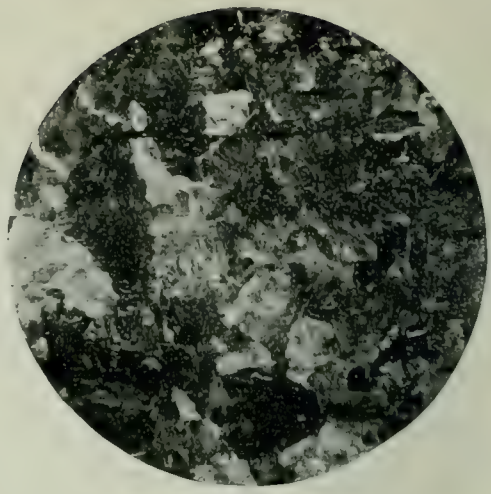

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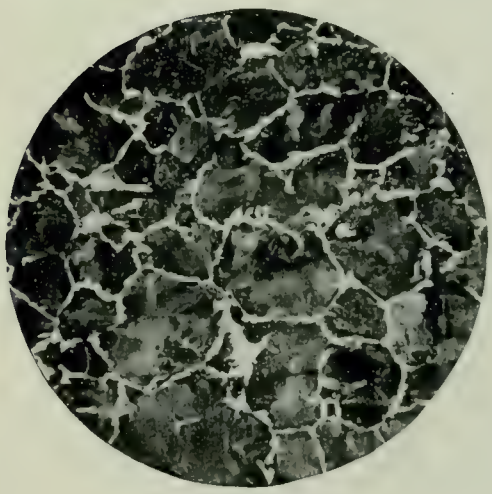

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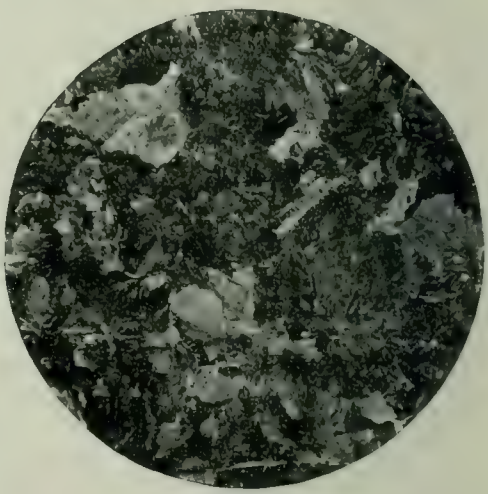

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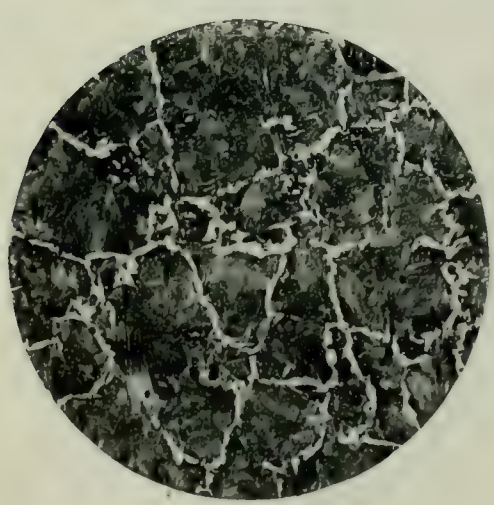

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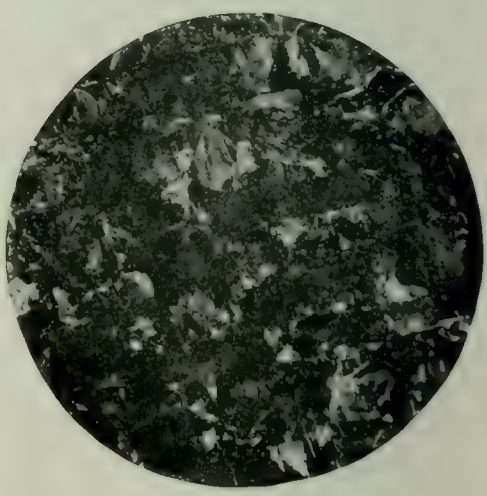

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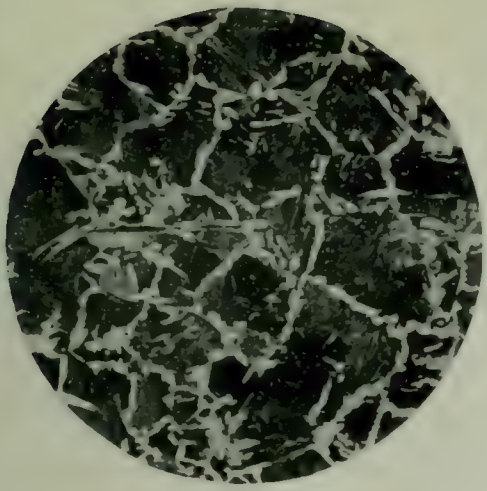
Fig. 13



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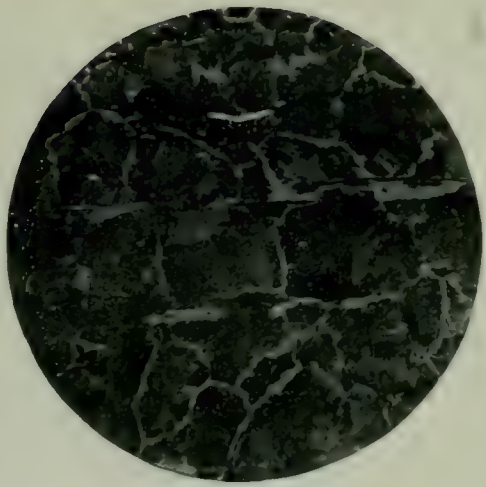

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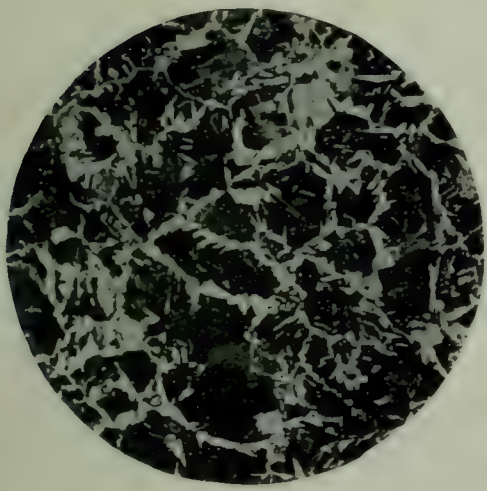

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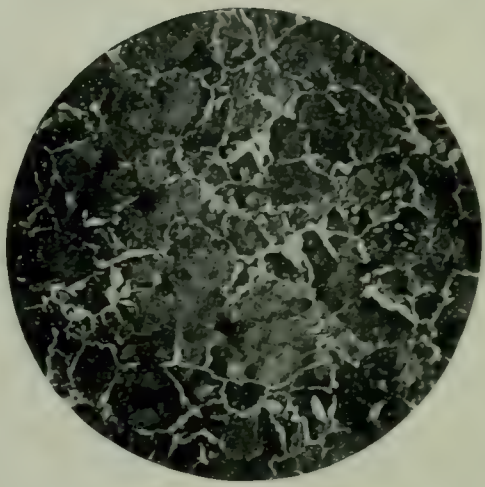

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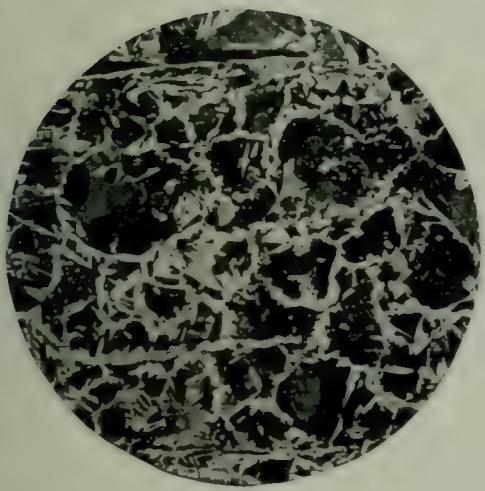

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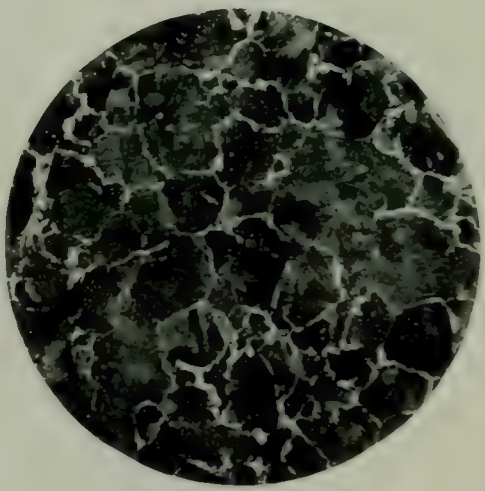

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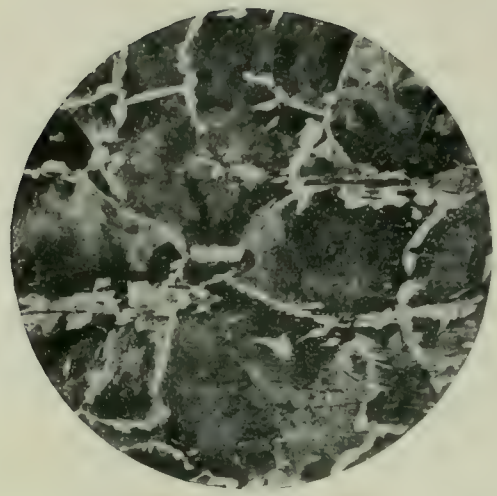
Fig. 14



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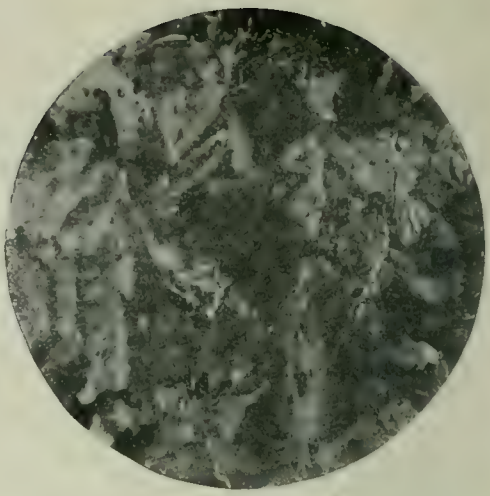

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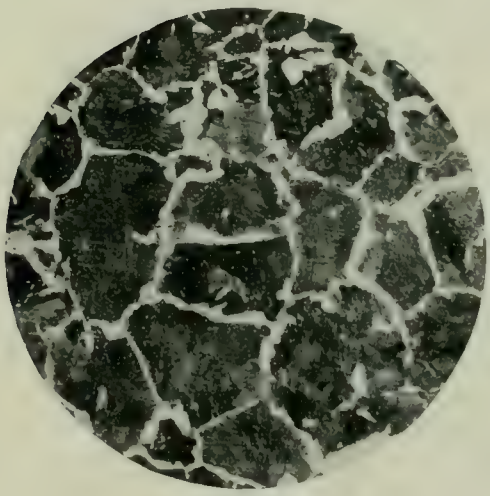

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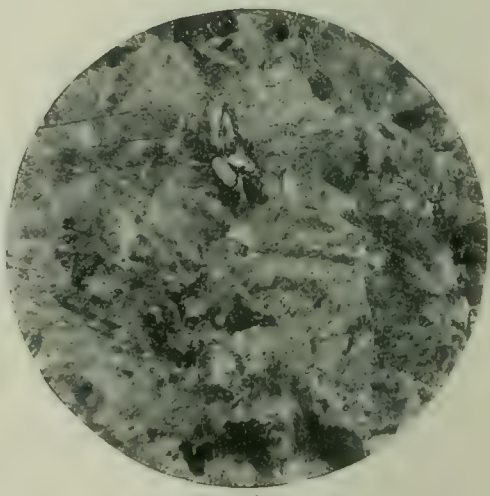

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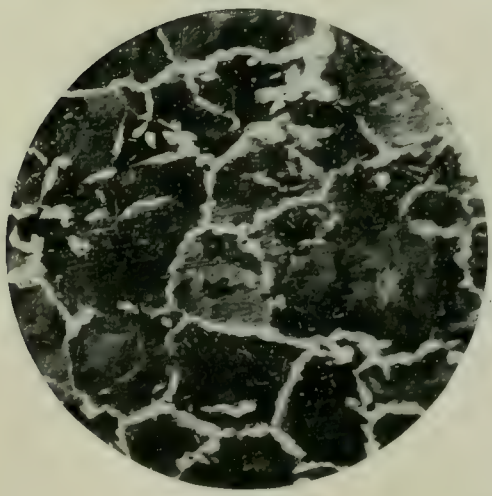

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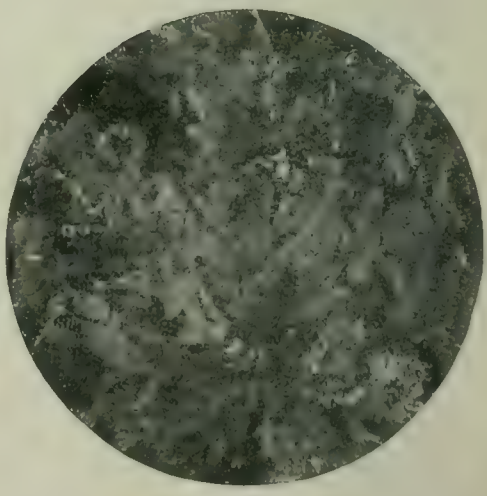

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Fig. 15

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 39

ANALYSIS OF PRINTING INKS

BY

J. B. TUTTLE, Assistant Chemist

and

W. H. SMITH, Assistant Chemist

Bureau of Standards

[JUNE 12, 1914]

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By J. B. Tuttle and W. H. Smith

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I. INTRODUCTION

Some years ago the Government Printing Office requested the Bureau of Standards to make an analysis of several of the printing inks which they were using. A search of the literature failed to reveal anything which would be of material assistance. The procedure which was devised for making these tests has been revised and amplified from time to time, and in the form in which it is given below has been in use for two or three years. The results of these tests have been so satisfactory that the procedure is now given in the hope that it may be of service to those who, without any previous experience, may be called upon to analyze printing inks.

II. COMPOSITION OF PRINTING INKS

In view of the fact that this bureau is now preparing a circular of information on the general subject of printing inks, it is not considered necessary to discuss here at length the composition of printing inks. In this circular it is proposed to give the composition of the more common types of ink, and those who are interested in this phase of the subject will doubtless find there the information they may need. Suffice it to say that the oil may contain linseed oil, mineral oil, rosin oil, hard gums, rosin, and soaps. The pigment of the black inks may contain ivory black, carbon black, lampblack, magnetic pigment (artificial magnetite), bone black, Prussian blue, aniline dyes and lakes, oil driers, and mineral fillers of various kinds. The pigments in the colored inks are usually the common mineral pigments and aniline lakes. A few qualitative tests will show which ones have been used.

III. PROCEDURE OF ANALYSIS

The purpose of the following scheme of analysis is to ascertain the approximate composition of the inks and to prove the presence or absence of injurious materials. It is therefore not at all necessary that the analysis shall be of the highest accuracy, and indeed it is just as well to admit now that with a mixture of as many materials as we have in printing inks such accuracy is entirely out of the question. Where two or more methods are available, preference is given either to that method which is the shortest, or which most easily permits of combination with methods for the determination of other constituents. The result has, on the whole, been very satisfactory, although there have been times when greater accuracy would perhaps have been desirable.

It is not necessary in every case to run through the entire scheme of analysis for any particular ink; frequently a few qualitative tests, combined with several practical tests on the press, will give all the information desired.

1. SEPARATION OF OIL AND PIGMENT

We shall first divide the components of printing inks into two classes, oils and pigments. Separation of these two is readily effected by means of the proper solvent, or a combination of solvents.

The first solvent tried was petroleum ether, which was found to be very satisfactory with certain grades of ink, particularly web-press and flat-bed inks, but with the better inks it gave a very poor separation. Ethyl ether and benzene were both tried and each had its good points, but the best results were obtained, all classes considered, by using a mixture of three parts of ether to one part of benzene. Separation by the method of settling was tried; adding the solvent to the ink in a tall cylinder, stirring thoroughly, and allowing the pigment to separate out after standing, decanting the clear solution and repeating with fresh portions of the solvent until all the oil was removed. This was found to be too long a process for satisfactory use. Centrifuging was then tried and found satisfactory. The method as finally adopted is as follows:

About 50 grams of ink (avoiding the hard film which frequently forms on the surface) is placed in a weighed glass tumbler of about 300-cc capacity, a small amount of solvent added, and the whole stirred thoroughly until a homogeneous mixture is obtained. The glass is then filled with the solvent to within about half an inch from the top, and the whole again stirred. It is next placed in the metal cup of the centrifuging machine, and the space between the glass and metal cups filled with water in order to equalize the pressure of the liquid inside the glass during the centrifuging. Placing a rubber disk at the bottom of the metal cup has been found to materially lessen the danger of breakage during the operation. The metal cup and contents are then exactly counterbalanced, most conveniently by either a second sample of the same ink or another sample of ink, and then both are placed in the machine. For web-press and flat-bed inks 2000 revolutions per minute for 10 minutes is sufficient for a complete separation. Where carbon black has been used it has frequently been necessary to run the machine at 2600 to 2800 revolutions per minute for 20 or 30 minutes before a satisfactory separation is secured. The clear liquid is decanted through a pleated filter into a glass bottle, a further quantity of solvent added, and the process repeated. Usually three treatments suffice to give practically complete separation of oil and pigment. The glass and contents are dried at about 90° C and on cooling

reweighed. The increase in weight is the pigment, which is calculated to percentage. The amount of pigment on the filter paper should be negligible if the centrifuging has been efficient.

This method will not always yield results of great accuracy. The errors, which vary in magnitude with different inks, are as follows:

Some of the dyes are soluble to some extent in the solvents, tending to give low results for pigment.

Hard gums may not be completely soluble, and thus part will remain with the pigment.

The hard scum (linoxyn) which forms on the surface of the ink after it has been exposed awhile, is difficultly soluble and remains with the pigment. This should be excluded in sampling, for if it is not done a considerable error may be introduced.

Carbon black contains some particles so fine that it is impossible to cause them to settle, even in the centrifuge.

The net error of this determination is therefore the algebraic sum of these various errors.

2. ANALYSES OF THE OIL

The oil fraction may contain linseed oil, hard gums, rosin, rosin oil, mineral oils, and bituminous substances. The last mentioned, when present, must be judged largely by their color; being a mixture of a number of different substances of varying chemical nature, the determination of the total amount present is a matter of too much difficulty to justify the time required.

Determining the various constants, such as iodine number, saponification number, acid number, etc., does not give very reliable data regarding composition. If there were but two components, the proportion of each might be determined at least approximately in this way, but with three, and sometimes more, substances present, such determinations are useless, even if the constants of the individual substances are well known. We are therefore forced to rely upon qualitative tests, supplemented by quantitative determinations of some of the more important constituents.

We have found it convenient to regard the oil fraction as consisting of hard gums, rosin, unsaponifiable matter, and linseed oil.

The hard gums are difficult to determine, the only method which has given any measure of satisfaction being that of McIlhenny.[1] This method depends upon the insolubility of hard gums in water and petroleum ether. The method is much better adapted for the analysis of paints than printing-ink varnishes, but it can be used for the latter to obtain some idea of the amount present.

The general procedure adopted in this Bureau, for the analysis of the oil fraction, is as follows:

Sufficient of the solution from the separation of the oil and pigment to leave a residue of about 5 grams is evaporated in a weighed beaker; 50 cc of normal alcoholic potash is added, the beaker covered with a watch glass, and heated on a steam bath for several hours, stirring frequently to assist saponification. When the latter is complete the watch glass is removed and the alcohol distilled off. The residue is transferred to a separatory funnel with successive portions of water, using in all about 100 cc, and extracted with petroleum ether until no further oil can be extracted. Four extractions are usually sufficient. The petroleum ether fractions are united in another funnel, washed with water until the wash water gives no further alkaline reaction, filtered into a weighed beaker, the petroleum ether distilled off, and the residue dried at 95° C, cooled, and weighed. If this unsaponifiable matter is over 2 per cent, it indicates the presence of something else than linseed oil and hard gums. The wash water from the first two washings should be united with the water layer in the first separatory funnel.

This unsaponifiable matter is tested for the presence of rosin oil. The most satisfactory method of testing qualitatively for this material is the Liebermann-Storch test, which consists in heating a small portion of the oil with 10 cc of acetic anhydride, allowing it to cool, and adding a drop of sulphuric acid, sp. gr. 1.63. A violet coloration indicates rosin oil. It is always best to run a check test at the same time with some pure rosin oil or rosin. The test is identical for the two materials.

If the test for rosin is positive, the alkaline water solution which has been extracted with petroleum ether is made acid with hydro-

[1] P. C. McIlhenny: Chem. Eng., 8, p. 70, 1908; Chem. Abs., 2, p. 2630, 1908.

chloric acid (there is usually sufficient dye present from the ink to act as indicator), and the fatty acids which are thus liberated are extracted with successive portions of ethyl ether. These extracts are united, washed free from acid and salts, and evaporated in a small beaker.

A quantitative determination of the rosin can be made by either the Twitchell method, which depends upon the separation of the esters of the fatty acids, or by Gladding's method,[2] which depends upon the separation of the silver salts of these acids.

A very satisfactory method, and the one which is used here, is the modification of the Gladding method suggested by E. J. Parry.[3] The fatty acids are dissolved in 20 cc of 95 per cent alcohol, a drop of phenolphthalein is added, and then strong caustic soda (one part alkali to two parts water) until the reaction is just alkaline. The solution is heated for a few minutes, allowed to cool, and then transferred to a 100-cc stoppered graduated cylinder. The latter is filled to the 100-cc mark with ether, 2 grams of powdered silver nitrate crystals is added, and the mixture shaken vigorously for 15 minutes, in order to convert the acids into their silver salts. When the insoluble salts have settled, 50 cc of the clear solution (containing the silver salts of rosin) is pipetted off into a second 100-cc cylinder, and shaken with 20 cc dilute hydrochloric acid (one acid to two water). The ethereal layer is drawn off, and the aqueous layer is shaken twice with ether. The ether extracts are united, washed with water, and the ether distilled off in a weighed beaker. The residue (rosin) is dried at 110° to 115° C, cooled, and weighed. The results are calculated on the basis of the original weight of the oil.

The difference between 100 per cent and the sum of the unsaponifiable matter (if over 2 per cent) and the rosin may be considered linseed oil.

3. ANALYSIS OF THE PIGMENT

(a) BLACK INKS

The first step in the analysis of the pigment of a black ink is to ignite a weighed quantity in a porcelain crucible (platinum can not be used on account of the lead which is usually present). The

[2] Am. Chem. J., 3, p. 416. 1881–82. [3] Allen's Commercial Organic Analysis, 4th ed., Vol. V, p. 73.

ignition should be performed at the lowest possible temperature required to obtain complete combustion. This precaution is general, and applies to all inks. The loss on ignition represents lampblack, the carbon of boneblack (should there be any present), aniline dyes, and undissolved oils or gums. Prussian blue is decomposed by heat, part of it being volatilized, the iron remaining as iron oxide. The residue from the ignition contains any added mineral matter of the pigment, lead or manganese from the driers, iron oxide from the Prussian blue, or iron oxide added as such (the so-called magnetic pigment), calcium phosphate if boneblack is present, and alkali or calcium carbonates from the soaps present. All ignitions of pigment must be performed under a hood having a strong draft.

The ash is analyzed quantitatively for insoluble matter, lead, iron, manganese, and calcium.

One-quarter gram of the ash is heated to dull redness in a porcelain crucible for a few minutes, cooled in a desiccator, and weighed. This is transferred to a 250-cc beaker, using concentrated hydrochloric acid to dissolve any material that may stick to the crucible. About 25 cc of concentrated hydrochloric acid is added, the beaker covered with a watch glass, and after heating until as much as will go in solution is dissolved, the cover is removed and the solution evaporated to dryness. The residue is moistened with a few drops of strong hydrochloric acid, 50 to 75 cc of boiling water added and the solution is filtered, washing thoroughly with hot water. The filter paper and residue are ignited and weighed, and the product is called "insoluble matter."

Fifty cubic centimeters of 10 per cent sulphuric acid is added to the filtrate from the previous determination and evaporated down until the solution fumes strongly. This is cooled, diluted carefully with about 100 to 150 cc of water, and heated on the steam bath until any basic ferric sulphate which sometimes separates is redissolved. The precipitate containing the lead sulphate is now filtered off. A small amount of lead sulphate will, in all probability, stay in solution, but inasmuch as the ash is seldom more than a few per cent of the entire ink, and of this only a

small amount is lead, the amount thus lost is negligible. The precipitated lead sulphate is dissolved in ammonium citrate or acetate, filtered from any insoluble matter, the filtrate made strongly acid with sulphuric acid, and the precipitated lead sulphate filtered off on a Gooch crucible, ignited, and weighed. We have used for this purpose a platinum Gooch crucible with a platinum felt, and found it extremely satisfactory. The insoluble matter from the ammonium acetate solution should be examined for calcium and barium.

Another method for the determination of the lead is to nearly neutralize the acid present with sodium carbonate, saturate the solution with hydrogen sulphide, filter off the precipitated lead sulphide, dissolve it in fairly strong nitric acid, and determine the lead as sulphate by the addition of sulphuric acid as above. In this case solution in ammonium acetate is omitted. The former method is of advantage where qualitative tests show that there is very little manganese present, and it is desired to determine only the iron. The filtrate from the lead sulphate leaves the solution in perfect condition for this determination. The iron is reduced to the ferrous condition by passing the solution through a Jones reductor, and the ferrous sulphate titrated with a standard solution of potassium permanganate, which has been standardized with sodium oxalate.

Iron is separated from manganese and other metals which may be present by precipitation with ammonia, the precipitate being filtered off, dissolved in hydrochloric acid, reprecipitated with ammonia, and again filtered. It is now dissolved in hydrochloric acid, sulphuric acid added, and evaporated down until all the hydrochloric acid is removed; the solution is diluted and the iron determined as before, with the Jones reductor. This method for determining iron is rapid and accurate. Before the addition of the ammonia, if hydrogen sulphide has been used, the solution should be boiled until all the hydrogen sulphide is removed, and nitric acid added to oxidize the iron to the ferric condition. In general, throughout the entire analysis, the usual precautions recommended by the various textbooks should be observed.

Hydrogen sulphide is now passed into the ammoniacal solution from the iron precipitation. This is allowed to stand over-

night, and the precipitate, if there is any, is examined for manganese. Usually there is only a trace of manganese, insufficient to warrant a quantitative determination. Should there be much manganese the sulphide can be filtered off, and the quantitative determination made by conversion into the pyrophosphate.

If it is desired to determine the calcium, this can be done after the filtration from the ammonium sulphide. (If phosphates are present—as, for instance, if bone black is present—a basic acetate separation is required.) In either case the lead should be separated by hydrogen sulphide. The filtrate from the manganese sulphide is heated on the steam bath until the hydrogen sulphide is removed, ammonia and ammonium oxalate are added, and the precipitated calcium oxalate is determined either as calcium oxide or sulphate.

The percentage of ash will be of great assistance in determining the nature of the pigment. Black oxide of iron is only slightly changed on heating, being completely oxidized to ferric oxide. Bone black is composed largely of calcium phosphate, yielding the greater part of its weight as ash. The presence of any large amount of phosphoric acid will be sufficient evidence that bone black has been used.

Prussian blue should be tested for qualitatively in the dry pigment. For this purpose 1 gram of pigment is moistened with 2 or 3 cc of normal alcoholic potash, heated on the steam bath until the alcohol is removed, 5 cc of water added, and the insoluble matter filtered off. The filtrate is made acid with hydrochloric acid, and filtered again if necessary. When ferric chloride is added, a blue precipitate will be obtained if Prussian blue is present. Sometimes sufficient blue dye goes through the filtrate to obscure the reaction. In this case the solution is again made alkaline and filtered. After filtration it is made acid with hydrochloric acid as before, and then copper sulphate is added. The precipitate is filtered and washed thoroughly. In this case we will have reddish-brown copper ferrocyanide. It is advisable, in case of doubt, to add a small amount of Prussian blue to the pigment, and make a check test.

In the absence of black oxide of iron we may assume that all of the iron in the filtrate is due to the Prussian blue. The per-

centage of Fe_2O_3 in the ash, multiplied by the percentage of ash in the pigment, multiplied by the factor 1.53, will give, roughly, the amount of Prussian blue present. The factor 1.53 is obtained by the ratio $Fe_7(CN)_{18}$ to Fe_2O_3. This is purely theoretical but is sufficiently accurate for the purpose.

Practically all of the dyes which are used in black printing inks are soluble in alcohol, so that an approximate determination can be made by extracting the dye with this solvent. For this purpose we have used an extractor of the Wiley type, in which the material is extracted by the solvent at its boiling point.

When the presence of oxide of iron is suspected, 1 gram of pigment is wrapped in filter paper and the dye extracted with alcohol, as in the preceding paragraph. When all of the dye has been extracted, the paper and contents are dried and the nitrogen is determined in the residue by the Kjeldahl method. From the nitrogen thus determined the Prussian blue is calculated, using the factor 3.41. The Fe_2O_3 present in this amount of Prussian blue, is deducted from the total Fe_2O_3 found in the ash. The remainder will be the percentage of iron from the magnetic oxide. The formula of the latter is theoretically Fe_3O_4, and the proper calculation should be made. This method for the determination of Prussian blue depends upon the fact that the aniline dye is the only other material which may contain nitrogen. Instead of calculating the Prussian blue from the amount of iron present, we determine it from the nitrogen remaining after the removal of the aniline dye. In this way both Prussian blue and magnetic oxide of iron may be determined with reasonable accuracy.

(*b*) **BLUE INKS**

A weighed quantity of pigment is ignited as under black pigments. The ash is analyzed by the same procedure as before, determining only lead, manganese, and iron if the qualitative tests show that Prussian blue is present. The lead and manganese are reported as metallic driers, the iron is calculated to Prussian blue, and the remainder reported as mineral filler. The composition of the filler, as a rule, is of no consequence.

The presence of ultramarine will be shown by the blue color of the ash. We have, unfortunately, no method for its quantita-

tive determination. In this case the ash is reported after deducting the lead and manganese.

Soluble aniline dyes are determined by extraction with alcohol, as under black pigments.

(c) RED INKS

The most brilliant red mineral pigment is unquestionably vermilion (mercuric sulphide). Its price prohibits its use in any but the best grades of red ink. It is very readily detected qualitatively by taking a small quantity of pigment, covering it with 4 or 5 cc aqua regia, and heating gently. This is diluted with five volumes of water, filtered, and stannous chloride added to the filtrate; a grayish precipitate of mercury will be formed if vermilion is present. A very small amount can be readily detected by this test.

The quantitative determination of vermilion, however, is much more difficult. The estimation of mercuric sulphide under the most favorable circumstances is a problem requiring both skill and experience. One method is to dissolve the mercuric sulphide in aqua regia, and after nearly neutralizing the diluted solution to precipitate the mercuric sulphide with hydrogen sulphide, and weigh the precipitate on a Gooch crucible, observing all the precautions to eliminate sulphur which separates during the precipitation.

The following procedure has also been found of value: One gram of the pigment is treated with a slight excess of ammonium sulphide. Sodium hydroxide is then added, while stirring. The beaker is placed upon the steam bath, adding more alkali if necessary, until all the mercuric sulphide has passed into solution. An excess of alkali should be avoided. The solution is allowed to cool, filtered, and the residue washed thoroughly. To the filtrate, sufficient ammonium nitrate to reprecipitate the mercuric sulphide is added, and it is then boiled to expel ammonia. The precipitate is allowed to settle, which takes but a short time, and the supernatant liquid decanted through a weighed Gooch crucible. The residual mercuric sulphide is boiled with a little sodium sulphite solution to remove free sulphur, and is then transferred to the crucible where it is washed with hot water until it no

longer reacts with silver nitrate solution. It is dried at 110° and weighed.

The pigment is ignited, and the ash analyzed for lead and manganese. The rest of the ash is reported as mineral filler.

(*d*) GREEN INKS

The coloring matter may be chrome green, green lake, or dye. Some of the darker shades are obtained by the addition of lampblack. The ash of the pigment is determined as usual. Part of this ash is taken and tested qualitatively for chromium. If present, the ash should be tested for the following substances: $PbCrO_4$, $PbSO_4$, PbO, $BaSO_4$, $CaSO_4$, Fe_2O_3, and Mn_3O_4. For the determination of sulphur, 0.250 gram of the ash and 5 grams of a mixture of equal parts of potassium nitrate and sodium carbonate are fused in a porcelain crucible over a sulphur-free flame. The cooled mass is extracted with hot water and filtered. The filtrate is acidified with hydrochloric acid, heated to boiling, and 10 cc 10 per cent barium chloride added. After standing overnight, the precipitated barium sulphate is filtered off, ignited, and weighed as usual. The solution should be sufficiently acid to prevent any significant contamination of the barium sulphate with barium chromate.

For the determination of barium, the insoluble matter is dissolved in hydrochloric acid, the solution made nearly neutral with sodium carbonate, and hydrogen sulphide is passed into the solution until all the lead is precipitated. The lead sulphide is filtered off, the filtrate heated to boiling, and 10 cc of 10 per cent sulphuric acid added. The barium sulphate is treated as directed under the determination of sulphur.

A fresh portion of ash is mixed with sodium peroxide and fused in a nickel crucible. The cooled melt is dissolved in hot water and filtered. Carbon dioxide is passed into the filtrate, and the latter heated again on the steam bath in order to precipitate any lead which may be held up by the caustic alkali. Any insoluble matter which may separate is filtered off. The filtrate is made strongly acid with hydrochloric acid, potassium iodide added, and the liberated iodine titrated with a standard sodium thiosulphate solution. From the amount of thiosulphate used the amount of CrO_3 present is calculated.

The two precipitates from the previous determination are combined and used for the determination of lead, iron, manganese, and calcium. They are dissolved off the filter paper with hydrochloric acid, the solution is nearly neutralized with sodium carbonate, and hydrogen sulphide passed into the solution. The precipitated lead sulphide is filtered off, dissolved in nitric acid, and determined as sulphate, as directed under black pigments.

The filtrate from the lead sulphide is heated until all the hydrogen sulphide is boiled off. If any sulphur separates, it is filtered off. Two or three cubic centimeters of nitric acid is added and the solution again heated. It is then made alkaline with ammonia and filtered. The precipitate is dissolved in hydrochloric acid and reprecipitated with ammonia, the precipitate again filtered off and the filtrate united with that from the first precipitation. This solution is reserved for the determination of manganese.

The second precipitate of iron is dissolved in hydrochloric acid, converted into the sulphate, and the iron determined as under black pigments by reduction with the Jones reductor and titration with potassium permanganate.

The united filtrates from the iron precipitation are saturated with hydrogen sulphide, allowed to stand over night, and then filtered. If there be a sufficient amount of manganese present, it can be determined quantitatively as pyrophosphate; otherwise qualitative identification will be sufficient.

The filtrate from the manganese sulphide can be used to test for calcium, as directed under black pigments, if this determination is desired. It is seldom of value.

It is difficult to give precise directions for calculating the results from the preceding determinations. To a large extent the analyst must use his experience in deciding the various questions as they come up. It is probably safe to assume that all of the chromium was present originally as lead chromate, and it should be so calculated. The iron oxide should be calculated to Prussian blue, provided there is a positive qualitative test. Any barium present should be calculated to sulphate; if there is any question as to its being originally present as carbonate, the ash of the pigment is treated with very dilute hydrochloric acid, the solution filtered, and the filtrate tested for barium. Barytes is difficultly soluble in

cold dilute hydrochloric acid. In the absence of barytes the sulphur present is calculated to lead sulphate. The excess of lead over that required for the lead chromate and sulphate may be considered as drier.

China clay may be present, either as an added part of the chrome green, or as the base of a green lake. In such cases the undetermined portion of the ash should be reported as mineral filler.

Green dyes are determined by extraction as usual. In the absence of chrome green the pigment is ashed, and the ash analyzed for lead and manganese only, the balance being reported as mineral fillers.

If lampblack has been used to produce a dark shade of green, it can be tested qualitatively by taking a small portion of the pigment, treating it with strong alkali, and filtering through a Gooch crucible, washing first with hot water, and finally with moderately strong hydrochloric acid. Lampblack will show a black residue, which will disappear on ignition. No quantitative determination has been developed for this material, and it is generally classed with the volatile constituents, which are then reported as aniline dye, lampblack, undissolved oil, etc.

(*e*) INKS OF OTHER COLORS

The above classes represent the inks most used for ordinary work. If it is desired to test other colors, the general procedure would be simply to make qualitative tests for the pigments. The metallic driers present can be determined in the ash if so desired. Reference to the various textbooks on this subject may be of assistance in suggesting what materials may be present.

IV. RELATION OF ANILINE DYES TO THE PAPER

The soluble aniline dyes used in printing inks are usually of only secondary importance. They are present merely to neutralize the yellow color of the oil, and thus produce a deep black. Exposure to direct sunlight for a few hours is usually sufficient to destroy their color, so that for permanence, in so far as light is concerned, we must depend upon the Prussian blue, and it is for this reason that emphasis has been laid upon the determination of the latter pigment wherever it is present.

In the addition of aniline dyes to printing inks, there are several points to consider. If the dye is soluble in the oil, the amount so dissolved will have its true color. Where undissolved dye is present, it is necessary to know whether the dry powder has the same color as the dye in solution. For example, some of the blue dyes are blue in the dry condition, but others have a bronze or even a greenish color. These latter tones are particularly objectionable in halftone work.

In general, we may say that it is imperative that we should know whether the dye added to the pigment will produce unsatisfactory results. Some years ago the Government Printing Office had an experience which illustrates this point. In printing illustrations from halftone plates it was noticed that some sheets had a decidedly brownish color, while other sheets, printed on the same press and with the same ink, were perfectly satisfactory. A thorough examination of both ink and paper revealed the fact that the brownish color was due to insufficient coating of the paper. Around each fine point in the printing a brownish ring was formed, owing to the absorption of the oil by the paper. The color was intensified by the fact that the ink contained a yellow dye, which was fast to cellulose. In thus taking away the oil from the pigment the latter was left on the surface of the paper in a loosely adhering condition, and was easily brushed off, revealing the paper which had been dyed yellow. In the case of the sheets showing the normal color the coating was sufficiently strong to resist the penetration of the oil, which therefore dried on the surface without any unsightly effect.

We have here a combination of faults. There should be no separation of oil from pigment, although it is apparent that with a proper grade of coated paper such separation will not occur. The dye used in the ink was equally objectionable; it should have have been blue, and not yellow, and the dye should not have been fast to cellulose.

This particular case has shown the necessity of knowing whether the dye has any effect on the paper. This test is made by dissolving some of the dye from the pigment with alcohol and placing in this solution pieces of cotton thread. The solution is heated on the steam bath for about five minutes, the dye poured off, and the cotton washed thoroughly with hot alcohol. If the dyes are

fast to cellulose, they can not be removed from the cotton by this washing process.

With colored inks the question of importance is frequently not so much what dye or lake has been used, and how much, but how permanent it is. Exposure to light is the easiest method for determining this. This test is performed by making some streaks on white paper with the ink in question. These should be about half an inch wide and about 10 inches long. The film of ink should be as thin as it is possible to make it, and should correspond as nearly as possible to the thickness of the film of ink used in printing. The sheet is allowed to remain in a dark place for 24 hours to dry thoroughly, and is then divided into three parts. The middle section is exposed to direct sunlight until the color changes, or until it is apparent that no change will take place, 50 to 75 hours being about the right length of time. The two outside sections are kept in the dark for the purpose of comparison. After the exposure is completed the strips are joined together in their original position, when it is possible to detect very slight changes in color. A number of inks can be tested on the same sheet if so desired.

Another method for determining the relative permanency of different samples of the same color has been suggested.[4]

Flat tints of each ink are printed as strongly as if they were to be part of a color job. These tints should be about 5 by 7 inches in size. They should then be cut out to this size. If a photometer scale is then made of five layers of fine tissue paper, each layer 1 inch narrower than the preceding, this will give five different thicknesses of tissue, each thickness presenting a band 1 inch wide and 7 inches long. Across these and about 1 inch apart should be glued three strips of opaque black paper 1 inch wide and 5 inches long, starting 1 inch from and parallel to one narrow edge of the tissue paper. The photometer thus made, and a printed sheet of the ink to be tested, are then put into a photographic printing frame, which has a plain glass in the front of it. The whole is then exposed to the sunlight with an ordinary photographic printing-out photometer until the total exposure has reached a certain value on the photometer scale (usually the last number). When the printed sheet is taken from the frame it will

[4] Private communication from H. R. Gaylord, and Mr. Averill, of the State Institute for the Study of Malignant Disease, at Buffalo, N. Y., through E. S. Moores, of the Government Printing Office.

be found to be divided into three unfaded areas, corresponding to the three opaque black strips and four faded areas, each divided into five 1-inch squares which have each received different amounts of light. By placing sheets of different printing inks of the same color in the frame and exposing to sunlight to the same photometer number, the relative permanency of the different inks can be seen at a glance.

The photographic photometer may be bought at any photographic supply house which sells to professional photographers. If desired, three inks may be tested at one time by cutting the printed flat tints into strips 2 inches wide and 5 inches long and placing them in the frame so that each has an exposed and an unexposed area.

V. SPECIAL TESTS

The foregoing tests cover practically all the important components of the common inks. A few other tests might be made in case of trouble that can not otherwise be located.

Volatile constituents in the ink can be determined by placing a weighed quantity in a shallow layer in a porcelain or glass dish and heating in an air bath for one hour at 105° C, cooling in a desiccator, and weighing. It is hardly necessary to take the precaution of drying in an inert atmosphere. These volatile constituents may be benzine, turpentine, benzene, etc.

Certain patents call for the use of sodium silicate (water glass) in the thickening of the oil. The alkaline nature of this substance would prohibit its use in the presence of blue dyes and Prussian blue. It will probably be found with the pigment, and is easily tested for by treating the pigment with boiling water, filtering off the undissolved material, and testing the filtrate with phenolphthalein. It can hardly be considered a desirable substance in printing inks.

VI. ACCURACY OF THE ANALYSIS

While it may be assumed that every analyst desires to work with the greatest accuracy, frequently this must be sacrificed to some extent in order to obtain results in the shortest practicable time.

The foregoing analytical procedure has been in use in this Bureau for several years, and the accuracy obtained has been all

that could be expected of this class of material. To attain a higher degree of precision would demand more time and care than the results would warrant. There is certain to be more or less variation in two lots of ink prepared by the same maker, and yet such differences would have little or no effect on the working qualities of the ink. If, therefore, the results obtained by the chemist check at least as closely as the manufacturer can duplicate his product, they should be considered satisfactory. That this is true of the analysis of printing ink is shown by the following statement, which shows how closely one may expect duplicate determinations to check:

Analysis of ink:	
Oil and pigment separation	0.5–1 per cent of the ink.
Ash of ink	0.1 per cent of the ink.
Oil analysis:	
Unsaponifiable matter	0.2–1.0 per cent of the oil.
Rosin (i. e., the true rosin acids)	0.5 per cent of the oil.
Analysis of pigment:	
Prussian blue	0.5 per cent of the pigment.
Analysis of ash:	
Determination of lead, iron, manganese	0.5–1.0 per cent of the ash.

It should be remembered that these figures would be materially less if calculated on the basis of the entire ink. For example, an error of 0.5 per cent in determining any of the constituents of the pigment would be only 0.1 to 0.2 per cent of the ink; 1 per cent of the ash would be from 0.02 to 0.1 per cent of the ink; and such accuracy is frequently more than is needed to judge of the quality of the ink. Probably a considerable part of the error is due to segregation, and the resultant difficulty in obtaining a true average sample.

VII. CONCLUSION

The authors wish to acknowledge their indebtedness to Dr. H. N. Stokes, formerly associate chemist of the Bureau of Standards, Dr. Peter Fireman, and E. S. Moores, of the Government Printing Office, for many helpful suggestions during the development of this procedure of analysis, and to H. R. Gaylord and Mr. Averill for the method for determining the relative permanency of the color in inks to which reference has already been made.

WASHINGTON, June 12, 1914.

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 40

THE VERITAS FIRING RINGS

BY

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and

G. H. BROWN, Associate Ceramic Chemist

Bureau of Standards

[JUNE 5, 1914]

WASHINGTON
GOVERNMENT PRINTING OFFICE
1914

THE VERITAS FIRING RINGS

By A. V. Bleininger and G. H. Brown

The object of the present work is the investigation of the influence of temperature upon the firing rings used in the "Veritas firing system," which is employed in a considerable number of potteries and other clay plants. These rings are placed in several parts of the kiln and withdrawn at different times during the firing. Their shrinkage gives an indication of the progress of firing. The rings are made of a clay body, approaching white ware very closely in composition, and are 2.5 inches in diameter and have an opening about 0.85 inch in diameter. They are made by pressing the clay body in the condition of moist dust, using a steel die and a screw press. The diameter of the ring is determined by means of a simple measuring device, in which the ring is held against two pegs by a lever pressed forward by a spring. The ring is thus held in position by three points. The extremity of the lever, which is about 8⅝ inches in length, moves along a scale, which is graduated into 60 equal divisions in an arc about 2⅞ inches in length. Any change in diameter is indicated in a magnified degree by the displacement of the pointer along the scale. The principle involved is, of course, not new and was employed most admirably about 140 years ago by the famous potter, Josiah Wedgwood, in the form of the pyrometer with which his name is associated. Many other similar devices have been proposed, and it is a well-known fact that shrinkage measurements have been used in the brick industry for many years as the most useful criterion of the progress of vitrification.

The present device was first described in detail by Marc Solon,[1] the inventor. Mr. Solon, in the article referred to, does not claim

[1] The Pottery Gazette, Oct. 1, 1905.

any great novelty in the principles of his method, but states that its advantages consist, first, in being able to determine the progress of the firing at any time by the withdrawal of rings from certain parts of the kiln, so that uniformity of burning may be maintained; secondly, the shrinkage numbers indicate the actual heat work being done upon the body, so that the rate of firing may be accelerated during the period when little contraction is taking place and retarded when shrinkage is proceeding at its maximum rate. In this manner the firing may be adjusted to the requirements existing at any time, which would not be possible by the use of a pyrometer unless the most suitable rate of firing were previously determined. It is evident that, like the pyrometric cones, the firing rings can not indicate temperatures. The more rapid the rate of firing the higher must be the temperature corresponding to the different shrinkage numbers, and vice versa. At the same time, however, it would seem desirable to correlate the indicated contraction values with the temperatures for different rates of heating in order to connect the use of these trials with pyrometer practice. This is the object of the present work.

One of the requirements of a standard of this kind, where the same composition is to be used in plants making all sorts of products and using many kinds of clays, must be a practically uniform rate of contraction, for it is evident that any decided irregularities in this respect would tend to diminish the accuracy and usefulness of the system. Such fluxes as lime must, therefore, be avoided in the body used for these test specimens. The best mixture would probably be that of a white ware body in which the predominating flux is feldspar. Such a body is composed of about 52 per cent of clay substance, 33 per cent of flint, and 15 per cent of feldspar. By increasing the amount of feldspar the range of the scale may be readily extended to porcelain.

In the preparation of such standards it is necessary also to have available large quantities of the raw materials, thoroughly mixed, so that no undue variations may occur. Such factors as the fineness of grain of the feldspar and flint must be maintained constant, as well as the methods of preparation and pressing. Any decided change in the raw materials would make it difficult

to coordinate new mixtures with the old one, as the rate of contraction might be changed. However, by careful experimenting it should be possible to produce stock the properties of which would check with those of the standard mixture.

Forty of these rings were calipered with a micrometer and the average diameter found to be 2.5065 inches. Measurement showed slight deviations from the circular shape but not sufficiently great to be corrected for in this work. The largest deviation in diameter was 0.0012 inch and the mean deviation 0.0004 inch. The weight of the rings varied from 48.55 to 50.70 grams, their thickness being, of course, of no consequence. The measuring scale has five divisions to the left of the zero point, so that somewhat larger rings than the standard size may be measured, although the specimens of each shipment are always of the same caliper. Each division of the scale corresponds to a mean value of 0.0054 inch, as measured upon the specimen. Measurements of the scale by means of a microscope comparator showed considerable and irregular variations in the graduation. The measurements of the rings in practice could be made with a device capable of greater accuracy, such as a modified micrometer caliper.

In determining the shrinkage of the rings at different temperatures the question of rapidity of firing was taken into consideration, and four firings were made at the constant rates of increase of 12.5, 16.6, 25, and 50° C per hour. The burns were made in one of the gas-fired test kilns of the laboratory, having a capacity of about 28 cubic feet. The temperature was controlled carefully by means of two thermocouples, one of which was connected to a recording and the other to a nonrecording Siemens-Halske millivoltmeter. The cold junctions were kept at the ice point. A suitable opening was provided in the wicket for the removal of the rings, two of which were taken out at each drawing temperature. Upon cooling, the rings were measured by means of a micrometer reading to 0.0001 inch and the instrument furnished by the manufacturer. Three readings were taken of every ring and the average of these used. The results of this work are compiled in Table 1.

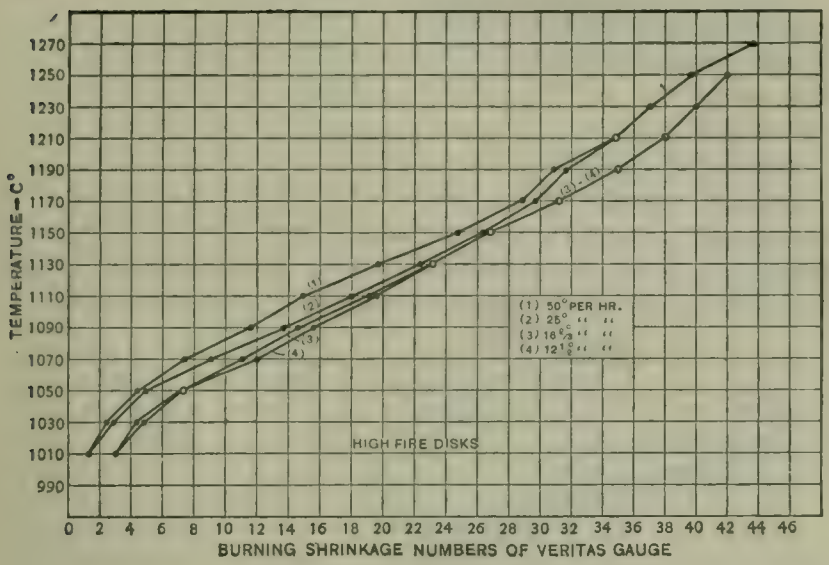
TABLE 1

Veritas Firing System—High Fire Disks

Temp. °C	Burning shrinkage (inches)				Shrinkage number			
	Rate, 50° per hour	Rate, 25° per hour	Rate, 16⅔° per hour	Rate, 12½° per hour	Rate, 50° per hour	Rate, 25° per hour	Rate, 16⅔° per hour	Rate, 12½° per hour
1010	0.0110	0.0124	0.0191	0.0208	1.37	1.50	3.00	3.50
1030	.0175	.0184	.0257	.0263	2.5	2.50	4.12	4.50
1050	.0279	.0303	.0403	.0395	4.37	5.00	7.12	7.00
1070	.0427	.0499	.0595	.0647	7.50	9.20	11.00	11.87
1090	.0636	.0746	.0785	.0823	11.75	13.75	14.75	15.87
1110	.0815	.0945	.1034	.1041	15.00	18.00	19.25	19.75
1130	.1035	.1183	.1205	.1201	19.50	22.25	23.00	23.00
1150	.1325	.1404	.1416	.1418	24.87	26.12	26.62	26.75
1170	.1525	.1571	.1680	.1656	28.75	29.25	31.12	30.75
1190	.1666	.1699	.1892	.1895	31.00	31.50	35.00	34.87
1210	.1863	.....	.2056	.2061	34.50	.....	37.75	38.00
1230	.2018	.....	.2198	.2175	37.12	.....	40.00	40.00
1250	.2165	.....	.....	.2297	39.75	.....	.....	41.75
1270	.2285	.....	.....	.....	41.50	.....	.....	.....

These values are also presented in graphic form in Figs. 1 and 2, in which the shrinkage is expressed in the numbers of the Veritas instrument and in inches, as measured by means of the micrometer caliper.

From the curves it appears that the rate of shrinkage is quite regular and that hence the composition answers the purpose for which it is intended very satisfactorily. Measurements were not taken at lower temperatures as these changes, as far as a body of this kind is concerned, are of no particular importance. It might be stated also that the instrument shows very distinctly that expansion occurs coincident with dehydration, though this point is not one of special significance as far as the control of burning is concerned. Upon comparing the four curves it will be noted that the time factor manifests itself in quite a marked manner, the temperatures at which equal contraction takes place being the higher the more rapid the rate of firing. These differences seem to diminish as the temperature rises. The firings at the rate of 12½ and 16⅔° per hour tend to coincide, as is to be expected, since the heat absorption approaches a constant value.


TEMPERATURE—C°
1270
1250
1230
1210
1190
1170
1150
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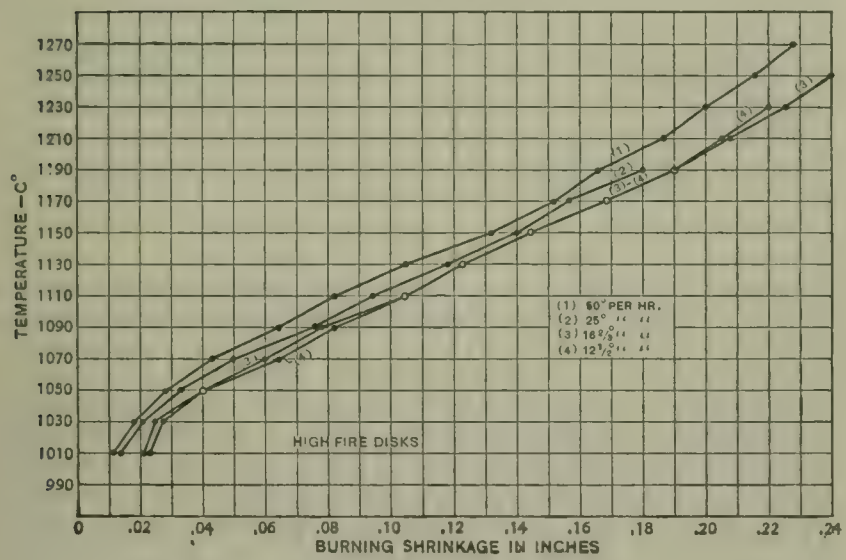
1110
1090
1070
1050
1030
1010
990
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46
BURNING SHRINKAGE NUMBERS OF VERITAS GAUGE
(1) 50° PER HR.
(2) 25° " "
(3) 16⅔° " "
(4) 12½° " "
HIGH FIRE DISKS

Fig. 1


TEMPERATURE—C°
1270
1250
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1110
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1050
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1010
990
0 .02 .04 .06 .08 .10 .12 .14 .16 .18 .20 .22 .24
BURNING SHRINKAGE IN INCHES
(1) 50° PER HR.
(2) 25° " "
(3) 16⅔° " "
(4) 12½° " "
HIGH FIRE DISKS

Fig. 2

In this connection it was thought desirable also to trace the connection between the porosity and the firing temperature, at the firing rates previously mentioned, which are coordinated in the diagram of Fig. 3. These show parallelism with the contraction curves and bring out the same evidence, though the curves are differentiated somewhat more sharply.

The firm placing on the market these pyrometric firing rings has brought out also a series intended to be used at lower temperatures. A set of these was tested by a method similar to that used for the higher temperature specimens, but using only the

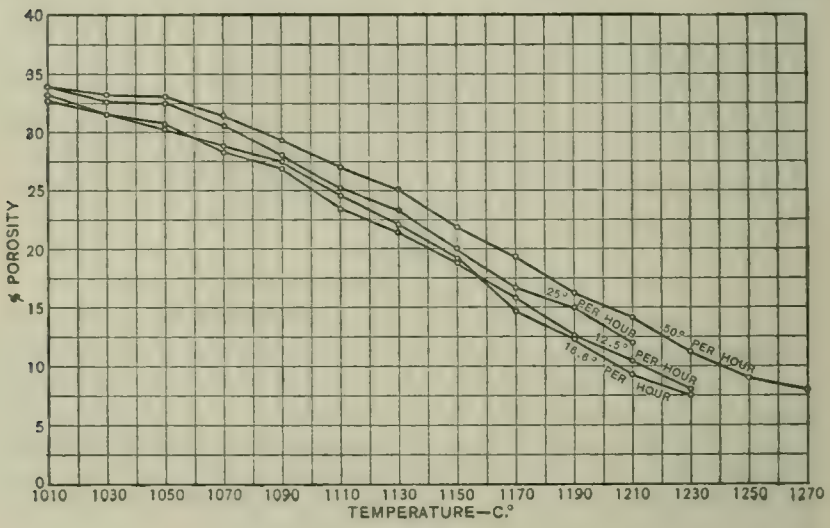

Fig. 3

12.5 and 25° per hour firing rates. The results of this work are presented in Fig. 4. From this curve it would appear that this series does not show a regular behavior throughout the temperature range in question. At least four rates of contraction may be observed. Between 950° and 1070° C the contraction progresses only very slowly, which is a serious drawback, as this particular temperature interval is a very important one for the firing of red burning clays. It would seem then that owing to this irregularity the accuracy of control would be seriously impaired within this interval, since the slight contraction indicated might

lead to the underestimation of heat effects bringing about all-important changes in the ware itself. It would be possible, however, to prepare a body which would show more consistent contraction than the one selected.

The standard firing rings of the higher temperature series are undoubtedly useful in controlling the firing of kilns, and if used in connection with a pyrometer would tend to make the latter a

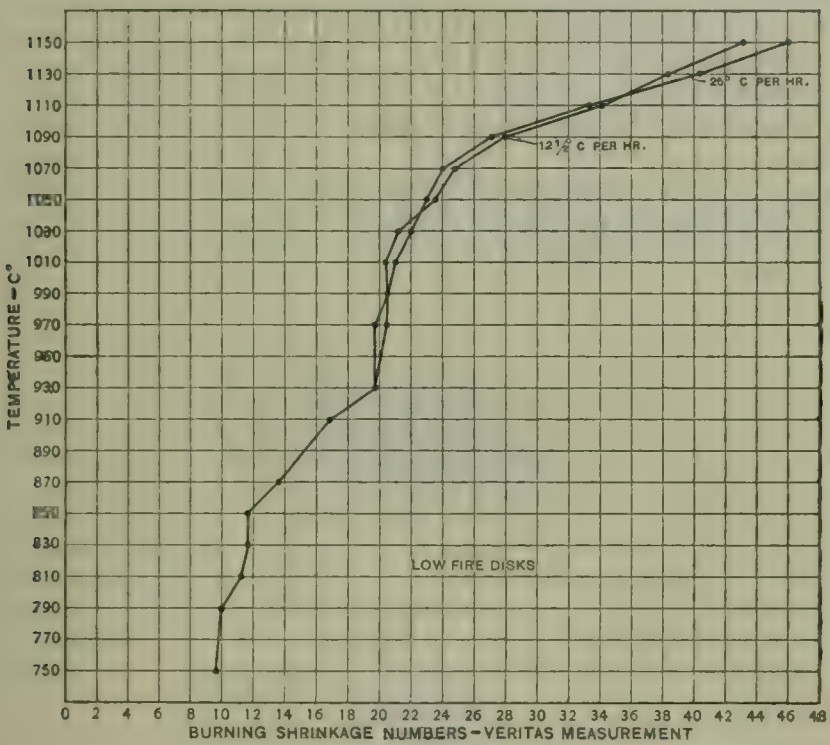

Fig. 4

far more valuable instrument. They offer a simple means of correlating heat work and the rate of temperature increase and their use in this connection would be very beneficial. The principle of the system is sound and the body selected has been well chosen for the firing of pottery kilns. The selection of the body for the lower series has not been so successful and, as has already been stated, there are serious objections to its use.

For the control of the burning of all kinds of clay ware, draw trials of this kind could be prepared from the clay or body of which the ware itself is made. It is evident that such specimens would be of greater service for determining the progress of firing than any other body. In order to make the trials comparable with each other they must of course be made from a well-mixed standard sample of the material and pressed under the same conditions. In this connection regularity of the shrinkage curve with temperature is not necessary, as it would be in the case of standards used in firing all sorts of clays. In fact, the very peculiarities of the contraction of such clay trials would be useful in checking the burning behavior of the same material made into ware.

Our thanks are due the Veritas Firing System Co. and the Trenton Potteries Co. for the supply of rings used in this work.

WASHINGTON, June 5, 1914.

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TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 41

LEAD ACETATE TEST FOR HYDROGEN SULPHIDE IN GAS

BY

R. S. McBRIDE, Associate Chemist

and

J. D. EDWARDS, Assistant Chemist

Bureau of Standards

[AUGUST 19, 1914]

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1914

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By R. S. McBride and J. D. Edwards

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I. PURPOSE OF INVESTIGATION

The regulations now in force in 10 States and in 27 large cities in other States regarding the purity of manufactured gas prescribe that the gas must be free from hydrogen sulphide or must contain not more than a "trace" of that substance. For the intelligent enforcement of such regulations definite knowledge regarding the significance of the various methods of testing for hydrogen sulphide in gas is necessary.

Many tests for hydrogen sulphide, both qualitative and quantitative, have been proposed. The test with lead acetate paper, however, has been almost universally used in gas testing, and it seems to be the one best adapted for that purpose. At the present time there is a wide variation in the method of carrying out this test. This lack of uniformity, together with the absence of definite information which would enable one to compare results of tests made in different ways, has given rise to misunderstanding and dissatisfaction. Some of the tests are designed to detect as small traces of hydrogen sulphide as possible, while others aim to give a negative test when a permissible amount is not exceeded. It is, therefore, necessary to understand the purpose of a given test before forming an opinion as to its merits.

The purpose of this investigation has been to study the effect of all of the important variables which may affect the results of different tests, in order to ascertain the relative sensitiveness of the methods and the minimum amount of hydrogen sulphide which can be detected by certain of these. It has also been our purpose to fix upon a definite test which should possess the following characteristics: It should be of suitable sensitiveness; it should be exactly reproducible; the apparatus necessary should be simple and inexpensive; and the method should be rapid and easy of application. It is desirable that such a test, although qualitative in principle, should be of quantitative significance.

II. PREVIOUS WORK

Only three papers have been found which bear directly upon the problem; these are by W. J. Dibdin and R. G. Grimwood,[1] R. Forbes Carpenter,[2] and Charles J. Ramsburg.[3] In the discussion of the first of these three before the English Society of Public Analysts the fact was brought out by Hehner that some additional work had been done by Dr. Rideal and by himself. However, so far as we have been able to determine, there are no published reports of this work. The methods employed, the results obtained, and the conclusions drawn in the three articles will be briefly summarized. The significance of this earlier work will be discussed in a later section of the present paper, on the quantitative significance of the various test methods.

1. DIBDIN AND GRIMWOOD

Dibdin and Grimwood employed for the preparation of their gas samples a 15-liter bottle, into which measured quantities of hydrogen sulphide were introduced and allowed to diffuse through the gas during a period of 30 to 45 minutes. Then, by inflating an india-rubber balloon, which was suspended from the rubber stopper in the neck of the bottle by means of a small glass tube, the gas was forced out of the bottle into the apparatus, where it impinged upon the lead acetate paper. When tests made on gas, taken from the top and bottom of the bottle, showed the same coloration, the mixing of the hydrogen sulphide with the gas was considered to be complete. When one series of tests had been completed, a gas of lower hydrogen sulphide content was made. A measured volume of the previous mixture was withdrawn and the residue washed out by passing coal gas through the reservoir until it gave no test for hydrogen sulphide. The measured volume of contaminated gas was then returned to the bottle, diffusion allowed to take place, and the gas reexamined. Successive dilutions were made to produce a gas mixture containing 1 volume of hydrogen sulphide in 10 000 000 000 volumes of gas.

[1] Analyst, **27**, p. 219; 1902. Reprinted in J. of Gas Lighting, **80**, p. 677; 1902.

[2] Forty-fourth Ann. Report on Alkali, etc., Works by the Chief Inspector, p. 81; 1907. Reprinted in J. of Gas Lighting, **103**, p. 167; 1908.

[3] Proc. Amer. Gas Inst., **4**, p. 453; 1909.

The test papers were dipped in a 12 per cent solution of lead acetate, held for a few minutes, while still wet, in an atmosphere of ammonia, then dried, and used in the dry condition. Table 1 shows the time required to produce a coloration when the gas impinged upon the paper at the rate of 0.5 cubic foot per hour.

TABLE 1

Tests Reported by Dibdin and Grimwood [4]

Grains of H_2S per 100 cubic feet of gas [5]	Volumes of mixture per 1 volume of H_2S	Time to give stain at different distances of paper from nozzle (minutes and seconds)			
		Close to—	¼ inch	½ inch	¾ inch
63	1000	At once	At once	At once	At once
6.3	10 000	0– 2	0– 4	0– 8	0–12
.25	250 000	0– 5	0–10	0–15	0–18
.063	1 000 000	0– 8	0–15	0–30	.....
.006	10 000 000	1– 7	1–30	1–50	2–20
.0006	100 000 000	5– 0	.....	12– 0	.....
.00006	1 000 000 000	11–30	.....	21–30	.....
.000006	10 000 000 000	>30	>30	>30	>30

[4] Loc. cit.

[5] The values given in this column have been calculated on the assumption that the original gas measurements were made at 60° F and 30" barometric pressure, in order to give an approximate idea of Dibdin and Grimwood's results in grains per 100 cubic feet.

In the discussion of this paper before the Society of Public Analysts objections were raised to the use of the rubber balloon, because of the difficulty of freeing the rubber from hydrogen sulphide, as reported by Dr. Rideal, who had used goldbeater's skin in its place. Mr. Helmer stated that it was his experience that the goldbeater's skin also rapidly removed traces of hydrogen sulphide. It was also stated that Dr. Rideal was able to detect 1 volume of hydrogen sulphide in 5 000 000 volumes of gas, passing the gas at 5 cubic feet per hour through the official Referees apparatus of the old form, in which the gas impinged upon the test paper. The time of exposure is not stated; but since the capacity of his gas reservoir was only 40 liters, he was limited to an exposure of about 15 minutes.

2. CARPENTER

The work reported in the Forty-fourth Annual Report of the Alkali Works Inspector was undertaken, in order to determine the reliability of the test for detecting hydrogen sulphide in the gases from chimneys and flues of chemical works. The method of preparing the gas mixture was, in general, the same as that employed by Dibdin and Grimwood; but in place of the rubber balloon, one made of gold-beaters' skin was employed, and air, instead of gas, was used for diluting the hydrogen sulphide.

The following samples of paper were prepared and tested:

1. "*Dry*" *paper.*—Schleicher and Schüll filter paper (No. 589, black band), soaked in a 12 per cent solution of lead acetate and dried at 80 to 90° C.

2. "*Moist*" *paper.*—Filter paper of the same quality, soaked in 12 per cent lead acetate containing 5 per cent of glycerin and partially dried. Paper damp to feel.

3. "*Moist* NH_3" *paper.*—Sample "moist" paper (2) held before use in fumes of strong ammonia.

4. "*Dry paper wetted with* NH_3."—Sample "dry" paper wetted, before use on lower half of strip, with concentrated solution of ammonia.

The test papers were held "either suspended by platinum wire or doubled to receive the gas centrally" in the exit tube, which "was expanded above into a cylindrical funnel with stopcock 3 inches long in the body and 1¼ inches diameter * * * A porcelain Gooch crucible served as a loose-fitting cap to the funnel and carried the wire that held the test paper." The procedure and results are described as follows:

In each test 1100 cc of gas were used, the time being five minutes, equal to 13 200 cc per hour (nearly half a cubic foot). The moment when a discoloration was first noticeable on the paper was recorded, as well as the final effect. The more important results obtained are summarized as follows:

TABLE 2

Tests Reported by Alkali Works Inspector[6]

Test paper	Volumes of mixture per 1 volume H_2S	Color noticeable in seconds	Color after 5 minutes with 1100 cc of gas	Smell
1. "Dry." Gas impinges centrally	100 000	At once	Black	Decided
2. Ditto. Strip suspended	100 000	30	Deep brown	Do.
3. "Moist." Strip suspended	100 000	30	Deep brown, rather lighter than No. 2	Do.
4. "Dry." Suspended	1 000 000		Faint brown	Slight
5. "Moist, NH_3." Ditto	1 000 000		Slight brown, deeper than No. 4	Do.
6. Ditto. Impinges	1 000 000		Deep brown	Do.
7. "Dry." Impinges	10 000 000		Remains white	None
8. "Moist, NH_3." Ditto	10 000 000		Slight stain	Do.

[6] Loc. cit. Only tests made in absence of sulphur dioxide are included, since the others have little or no bearing upon the question under consideration. It may be noted, however, that: "Sulphur dioxide renders the lead paper test less sensitive to sulphuretted hydrogen. The effect commences with a concentration, SO_2, 0.5 grain per cubic foot (= volume SO_2 per 2500 volumes), and increases with the proportion of sulphur dioxide present."

From a consideration of all the facts, of which the examples recorded above are typical, the following conclusions were drawn with respect to the results obtained by the described procedure:

1. *Condition of test paper.*—With gas up to 1 volume H_2S in 100 000 the condition of the test paper does not greatly affect the amount of discoloration. "Dry" paper, "moist" paper, and "moist NH_3" paper are about equally sensitive with suspended strip.

With gas 1 volume H_2S in 1 000 000 and upward, "moist NH_3" paper is most sensitive, and should alone be used.

2. *Direction of current.*—The test is far more sensitive when the gas is made to impinge directly on the surface of the paper. Thus, "moist NH_3" paper is only slightly discolored by air containing 1 volume H_2S in 1 000 000, when the flow is parallel to its surface; it is deeply stained when the gas impinges.

3. *Quantitative significance of results obtained with suspended strip.*—Stains of equal depth are obtained under the same conditions as regards quality of test paper, direction, and rate of flow of gaseous current, and proportion of sulphuretted hydrogen present.

Other conditions being equal, if the strength of gas be varied, the discoloration is greater as the proportion of sulphuretted hydrogen is increased, the difference of color obtained with gas 1 H_2S in 10 000, 20 000, 50 000, 100 000, etc., being easy to distinguish.

The limit of sensitiveness for "dry" paper is about 1 H_2S in 1 000 000; for "moist NH_3" paper, 1 H_2S in 10 000 000 with suspended strip.

3. RAMSBURG

The paper by C. J. Ramsburg reports on a number of tests, which were made to show the great difference in the intensity of color produced, when testing a given gas according to a number of different methods, as carried out in certain States and cities. It also contains a history of the subject of sulphur regulation in England, and gives the various official tests for total sulphur and hydrogen sulphide which have been used by the London gas Referees. The question of sulphur regulation, with particular reference to hydrogen sulphide, as followed in the United States, is discussed, and a number of State and municipal regulations on the subject are quoted.

The water in a 50 cubic foot gas holder was saturated with foul coal gas from which tar and ammonia had been removed, and by filling the holder with clean gas and allowing it to stand a gas was obtained which contained 0.53 grain of hydrogen sulphide per 100 cubic feet. The hydrogen sulphide was determined by absorption in an acid solution of cadmium chloride, the precipitated sulphide filtered off, oxidized to sulphate, and weighed as barium sulphate. Photographs are given of the test papers secured when testing this gas by the following six methods.

The test prescribed by the New York State commission, which was to hold a paper moistened with lead acetate in a current (or jet) of gas flowing at 5 cubic feet per hour for 30 seconds, showed a distinct coloration. Ramsburg evidently obtained this test with the gas impinging from a jet onto the paper, as may be seen from the form of stain shown in the photographic record of his results. The commission rule, quoted by him, provides for exposure to a "current of gas;" but the State law for second-class cities, not quoted, specifies exposure to a "jet of gas."

A stain of about the same depth as produced by the New York method was obtained with the "Connecticut test," which Ramsburg made "by allowing a stream of gas to flow through a round orifice not larger than $\frac{1}{32}$ of an inch in diameter, under a pressure not greater than 1.5 inches of water, and to impinge on a paper moistened with a solution of acetate of lead, placed at a distance of 1 inch from said orifice for a period of three minutes."

According to the "Boston method" a moist paper is held "in a small stream of gas ½ inch from the orifice for 60 seconds." A dark stain was produced when the test was carried out in this manner.

The present "London Gas Referees method," according to which a moist paper is suspended in the Referees apparatus (see Fig. 11) for three minutes, the gas flowing at the rate of 5 cubic feet per hour, showed no test in one minute; but a "rather distinct" test was obtained in three minutes, the color being, however, much lighter than in the three previous tests.

The "London Gas Referees method," used previous to 1906, specified the passage of 10 cubic feet of gas at the rate of 0.5 cubic foot per hour, the gas impinging on the paper. The test paper produced by this method was very dark.

The "Milwaukee method," which was to pass gas at the rate of 5 cubic feet per hour for one and one-half to two hours, through a piece of glass tubing 1 inch in diameter containing the test paper, also produced a deep black stain.

In the discussion of this paper before the Institute it was the opinion of many that the present tests were too sensitive. It seemed desirable to some to permit 1 grain of hydrogen sulphide per 100 cubic feet of gas; but such a specification would preclude the use of the simple tests, which are easy and quick of application. For this reason a qualitative method, the results of which would be roughly quantitative, was desired.

III. OUTLINE OF INVESTIGATION

From a consideration of the various methods used commercially for the detection of hydrogen sulphide and of the results obtained by the experimenters whose work is summarized above, as well as of preliminary tests made at the Bureau, the following variables were shown to be factors which must be considered in the investigation of these testing procedures:

1. The paper: Kind; method of its preparation, including the strength of lead acetate solution used, and the moisture content when used.

2. The gas: Its humidity, and the period and rate of flow.

3. The apparatus: Its form and size, as determining the circulation of gas with respect to the paper.

With gas mixtures containing various known amounts of hydrogen sulphide the several factors were studied one at a time; and results were obtained which indicate both the quantitative and the relative significance from an engineering or economic standpoint of the various methods of testing. It is hoped that this information will bring about a better understanding of the limitations which the various methods impose upon the gas maker. Having established the significance of the tests and the effect of the numerous variables, we have drawn up the specifications which are proposed for testing apparatus and methods.

IV. APPARATUS AND METHOD

1. PREPARATION OF GAS MIXTURES

One of the greatest difficulties met with in the study of the lead acetate test has been the preparation of a uniform gas mixture containing a known amount of hydrogen sulphide. None of the previous methods employed for this purpose, except that used by Ramsburg, has been free from very serious objections. For our work it was necessary to prepare 5 to 10 cubic feet of gas containing hydrogen sulphide in any desired amount. The following method of making such gas mixtures was devised:

The principle of operation is the mixing of known amounts of hydrogen sulphide, contained in some easily volatile solvent with known volumes of gas, this operation being conducted continuously and uniformly in the apparatus shown in Fig. 1. The gas first passes through a large tower A filled with sticks of potassium hydroxide, where any hydrogen sulphide originally present in the gas is removed. It then passes through the pressure regulator B, the wet meter C, and the glass tube F into the 30-liter mixing bottle H. The tower D, through which the gas could be

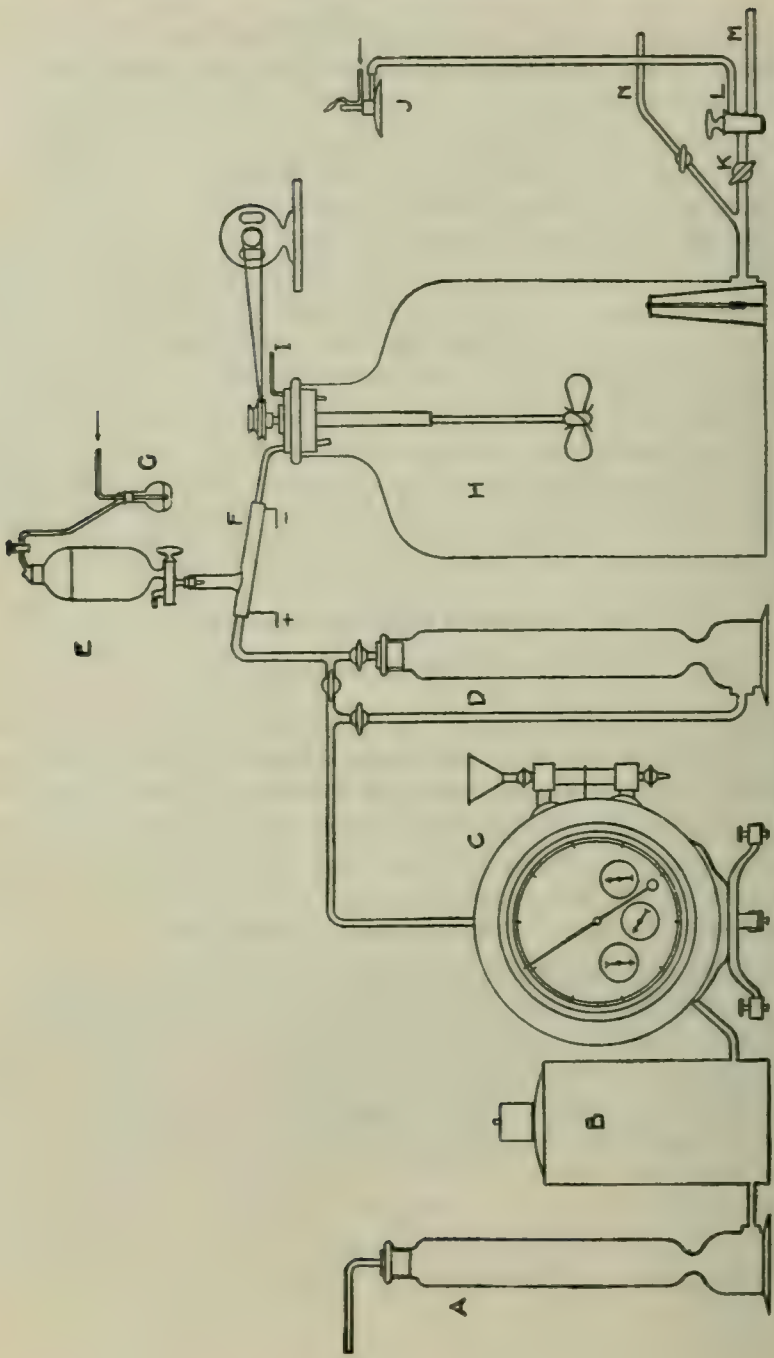

FIG. 1.—*Apparatus for preparation of gas mixtures.*

by-passed, served to dry the gas when desired. The solution of hydrogen sulphide in some solvent such as ether is held in the burette E, the tip of which is introduced through a rubber stopper into the side tube attached to F. The top of the burette is closed by a ground glass stopper to which is sealed a small stopcock. When a gas mixture is being prepared the solution is placed under slightly increased air pressure, and the stopcock at the bottom of the burette is adjusted so that the solution drips into the tube F at about 1 drop per second. The tube F, through which the gas passes at a uniform rate, is warmed by a small electric-heating coil, so that the hydrogen sulphide and its solvent are volatilized and carried along by the gas into the mixing bottle where a fan insures a thorough mixing. The increased pressure on the surface of the solution, necessary to make it drip regularly from the tip, is secured by bubbling air through a small wash bottle containing some of the same solution, the air being so regulated that one bubble enters the wash bottle for each drop of solution that leaves the burette. The pressure in the large mixing bottle is ascertained by a U gage attached to the small tube I, and the temperature is obtained from the thermometer suspended before the gas outlet at the bottom of the bottle.

After the gas has been thoroughly mixed in the large reservoir, it passes to a three-way cock L by means of which it may be diverted to the burner J, which has a pilot light, or else to the apparatus under test, which is attached to M. The operation is thus continuous, the gas mixture being used at the same rate at which it is prepared either by burning at J or in the test apparatus, both branches being adjusted to give the same rate of flow. This rate of flow is adjusted to suit the pressure in the mixing bottle by means of the cock K, placed just before the three-way cock L. A small portion of the gas can be withdrawn for analysis through the tube N, to which is attached a five-bulb absorption tube and a wet meter in series (not shown in figure).

When starting a run, the burette, filled with ether in which the amount of dissolved hydrogen sulphide has been determined, is placed in position and adjusted so that the solution drops at a uniform rate. The gas flow is also properly adjusted, and the

gas mixture burned at J for 45 to 60 minutes to insure a uniform and constant mixture in the mixing bottle. When tests with lead acetate paper, made from time to time, show that this condition has been reached, the mixing operation is stopped so that the burette may be detached and weighed and the meter reading taken; the mixing is then again started. The weight of the burette and the meter reading are again obtained at the end of the run. From the weight of hydrogen sulphide solution introduced and its strength and the volume of gas plus ether through which it has been distributed, the hydrogen sulphide content of the gas can easily be calculated. A small portion of the gas is withdrawn through N, and the contained hydrogen sulphide absorbed in a solution of cadmium acetate.

The precipitated cadmium sulphide is then determined iodometrically. The determination of the hydrogen sulphide in the ether solution and in the gas is fully discussed on page 36 ff.

2. METHOD OF COMPARISONS

Having available a gas mixture, the hydrogen sulphide content of which could be controlled and kept uniform for any desired period up to several hours, we were able to make tests in which any one factor could be changed at will, while all others were maintained constant. Comparisons of sensitivity of one procedure with another were, therefore, easily obtained with a gas of any desired strength.

Since preliminary work indicated that the simple hydrogen sulphide tester (see Fig. 10) which was later chosen as standard, had a number of advantages over the other forms investigated, this apparatus was used in the study of the variables introduced by changes in the paper and in the gas, groups 1 and 2 indicated on page 11. When various forms of apparatus were being compared, they were connected in the set-up in parallel in such a way that the gas could be diverted to one or another at will. Comparisons between one procedure and another could thus be made very rapidly. No effort was made to have the same quantity of hydrogen sulphide present in the gas on different days. It is therefore not intended that comparisons should be made from one chart to another.

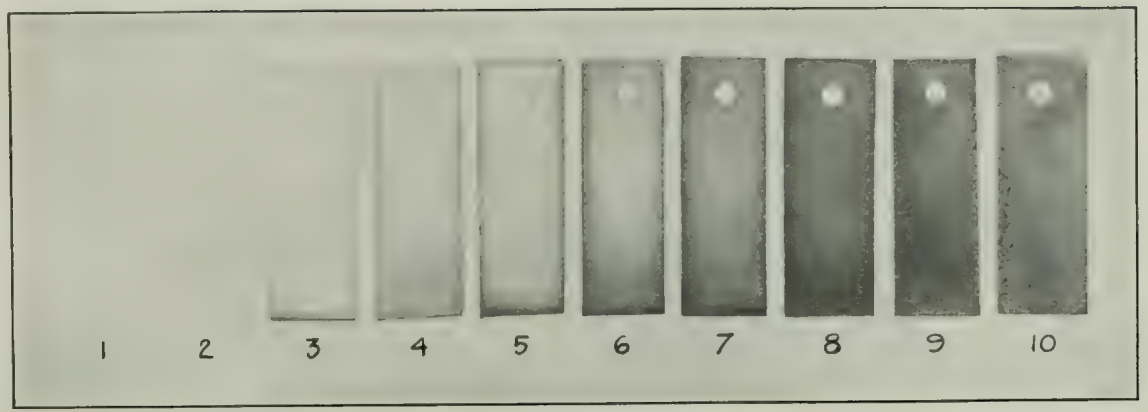

FIG. 2.—*Standard color chart*

To insure the uniformity of the gas supply throughout the period of any one series, control tests were run. These tests were made from time to time, and practically no difficulty was found in maintaining the mixture so uniform as to give exactly comparable results throughout any series.

3. RECORDING OF RESULTS

The problem of recording results offered a number of difficulties, the most serious of which was due to the impossibility of giving an accurate and brief verbal description of a test paper after exposure. The uncertainty which any such description leaves in the mind of a reader is well illustrated by the results reported by Carpenter. (See p. 8.) Therefore a photographic record of the tests was made. Test papers illustrated in any one plate are generally comparable; but care must be exercised in comparing the test papers shown in the different figures, because the proper relative depth of coloration is very difficult to secure in illustrations made by photographic processes. It should be particularly noted that a very light-brown coloration may appear quite dark when photographed, and may even appear to be black. On the other hand, some papers, showing a denser but silvery coloration, reflect more light than others less dense but of a brownish character; and, consequently, when photographed, the former may appear relatively too light.

To make it possible to record approximately the depth of coloration produced in any test, and thus give a basis for comparison of tests made on different days, a standard color chart was prepared. (See Fig. 2.) In making this chart a series of ten test papers was selected to form a graduated scale of colors, ranging from No. 1, which is a blank, not having been exposed to the gas, to No. 10, which is a very dark brown, so heavily stained that it shows some tendency to appear silvery and, hence, appears much lighter in color, relatively, than otherwise. Standard color No. 2 was selected as having as faint a coloration as could be easily distinguished without comparison with a blank paper.

Since test papers fade somewhat on keeping, those used for the standard-color chart were selected from a lot which had already aged for some time, so that further changes in color would be

slight and would have but little influence on the usefulness of the chart as a means of comparing results. The colors were selected strictly empirically and have no significance as representing definite amounts of hydrogen sulphide, except as the tests described below give some significance to them.

As tests were made the papers were matched as closely as possible with the standard colors and then dried in a dessicator in order to reduce fading to a minimum. When a series had been completed the test papers were mounted on cardboard and photographed. When thus mounted, differences in depth and character of the colors could be distinguished more easily than when unmounted, since the papers lay flat and there were no interfering shadows. This system of recording results proved very satisfactory.

V. VARIATIONS IN TEST PAPER

1. KIND OF PAPER

The kind of paper used is not without influence on the accuracy of the test. Among the factors that affect the ease with which slight differences in color may be distinguished are: The tint of the paper, the character of its surface, whether it is smooth or matte, the thickness and opacity, and the change in opacity brought about by moistening.

The most satisfactory paper to use is a hard, smooth, and fairly opaque filter paper of even thickness. Schleicher and Schüll's hardened filter No. 575 was found to be most satisfactory for our purposes and was used in making all tests. Test papers of this kind have the same general appearance when moist as when dry, so that a moist paper could be compared with the standard colors conveniently. None of the other papers tested was satisfactory in this respect.

The difference in appearance noted, when the same gas was tested in the same manner with different kinds of paper similarly prepared, is illustrated in Fig. 3 and described in Table 3.

FIG. 3.—*Appearance of tests made on different kinds of paper*

(Described in Table 3)

TABLE 3

Appearance of Tests Made on Different Kinds of Paper

(Illustrated in Fig. 3)

[All tests were made with moist paper, which had been prepared by dipping in 6.5 per cent solution and blotting, using the standard apparatus, with gas flowing at 5 cubic feet per hour for one minute.]

Test	Description of paper
181B	S. and S. "No. 575 hardened"; opaque with hard, smooth surface.
197	S. and S. "No. 602 extra hard"; surface rougher than No. 575.
198	S. and S. "No. 595"; lighter and softer than either of the above.
199	Rough qualitative filter paper with irregular, ribbed surface.
200	Smooth tablet paper; not as absorbent as the filter papers.
201	Paper towel with faint greenish tinge.
208	S. and S. "No. 575 hardened"; soaked in lead acetate for two minutes, otherwise same as for test 181B.
209	S. and S. "No. 589 blue band"; a thin soft paper, hard to handle without tearing when moist.

Greater differences in the appearance of the papers were noticed than are indicated by the figure and considerable change in the coloration of some of the papers occurred on drying. Only a few generalizations as to the kind of paper are needed, since each observer should satisfy himself that the paper used is suitable for the work to be done.

The following points, although not of great importance, are worthy of mention as a guide in the choice of paper:

1. Any paper having a yellowish tinge tends to obscure the first appearance of a stain when comparison is made with an unexposed piece of the same paper.

2. Papers with a rough matte or wrinkled surface are not as satisfactory as those with a smooth surface, since the rough surface adds an element of uncertainty to the test; but a shiny surface is not desirable.

3. Test papers 197, 198, and 199, which are typical of those made on filter paper with a rough surface, appeared slightly darker than paper 181 when moist, but lighter after they had dried out. This change in appearance on drying seems characteristic of the rough papers.

4. A transparent paper of uneven thickness, if viewed against certain backgrounds when moist, shows more of a coloration than a less transparent paper similarly treated.

5. When there is question as to the result of a test, the test paper should be compared with a piece of paper which has been similarly treated, but not exposed to the gas, the comparison being made with the papers in a good light and held against a white opaque background.

2. CONCENTRATION OF LEAD ACETATE SOLUTION

Results of tests made to determine the effect of varying the concentration of lead acetate solution with which the paper is treated are illustrated in Fig. 4, and the details of the tests are given in Table 4.

TABLE 4

Effect of Concentration of Lead Acetate Solution

(Illustrated in Fig. 4)

[All tests were made with paper exposed in the standard apparatus with gas of approximately 0.7 grain hydrogen sulphide per 100 cubic feet of gas. Paper B was dipped in the lead acetate solution, blotted, and used moist; paper D was dipped, dried, and used dry.]

Tests with paper B				Tests with paper D			
Test	Time (minutes)	Concentration of solution (per cent of lead acetate)	Color produced (standard color No.)	Test	Time (minutes)	Concentration of solution (per cent of lead acetate)	Color produced (standard color No.)
83	0.5	2		84	0.5	2	
85	0.5	6.5	3–4	86	0.5	6.5	2
87	0.5	12		88	0.5	12	
89	1	2		90	1	2	
91	1	6.5	5–6	92	1	6.5	3
93	1	12		94	1	12	
95	3	2		96	3	2	
97	3	6.5	6–7	98	3	6.5	5–6
99	3	12		100	3	12	

The papers illustrated in the three horizontal rows of this figure, which were exposed for one-half, one, and three minutes, respectively, show the effect of increasing time on the depth of color produced. However, the first three papers of each row, which were treated with 2, 6.5, and 12 per cent solutions of lead acetate, respectively, then blotted, and used moist, show how small an effect is produced by changing the concentration of the solution. The second three papers, which were treated in the same manner as the first three, except that they were dried before use, also show this effect to be very small.

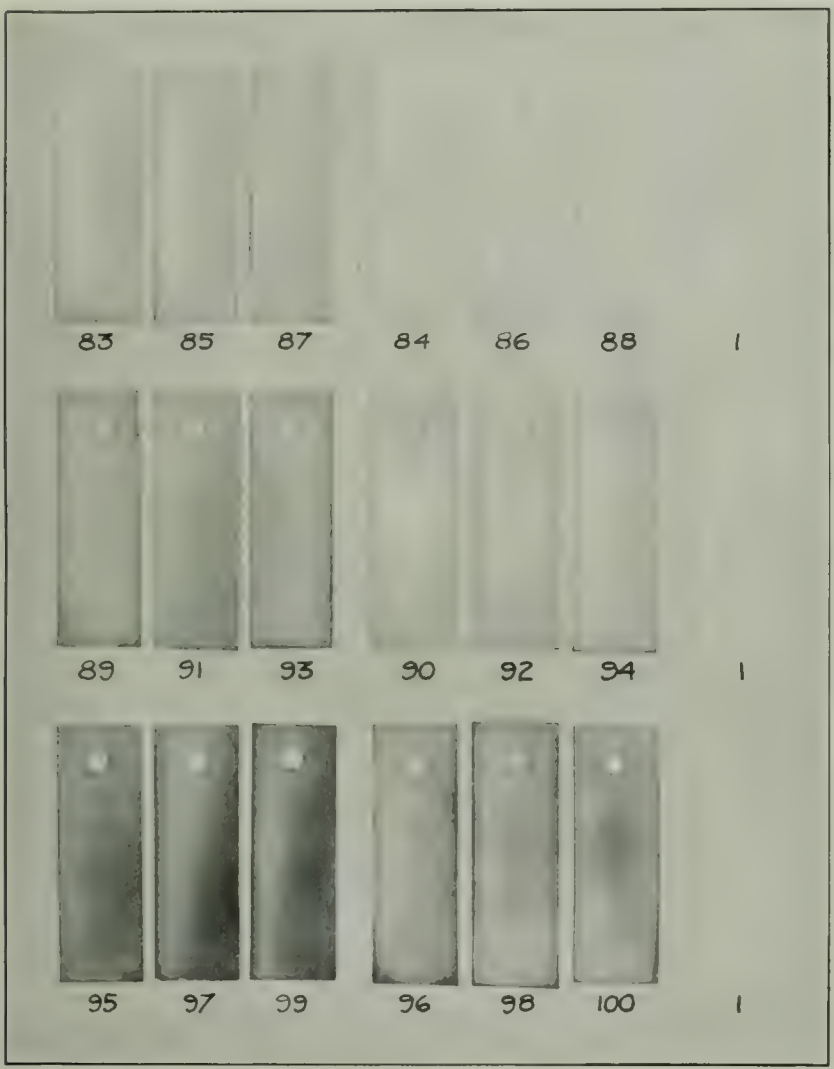

FIG. 4. *Effect of concentration of lead acetate solution*

(Described in Table 4)

Since the paper, even with the 2 per cent solution, holds a large excess of lead acetate over that necessary to precipitate the hydrogen sulphide coming in contact with it, it is not surprising that little difference is to be noted in the sensitivity of the test when different concentrations of lead acetate solution are used, although there seems to be a tendency for the paper treated with the 2 per cent solution to be slightly lighter in color than the other two.

Dibdin and Grimwood from a comparison of "papers soaked in various strengths of lead salts in solution * * * decided to adopt a paper prepared by moistening with an approximately 12 per cent solution of lead acetate." They do not state their reason for the choice, and the above-described results give no basis for any preference within the limits investigated.

The use of a 6.5 per cent solution corresponds to both American and English practice, arising from the old English rule which called for 100 grains of crystallized lead acetate dissolved in 100 cc of water. The 6.5 per cent solution was used for the bulk of the experimental work presented in this paper because of its previous wide use. However, a 5 per cent solution would give the same results and its use is recommended.

3. PREPARATION AND CONDITION OF PAPER

Papers dipped in a 6.5 per cent solution of lead acetate were treated in eight different ways, in order to ascertain the effect of varying preliminary treatment and moisture content at time of use. The papers used are described in the following tabulation, which also indicates the letter by which each paper is identified in the description of later tests.

A. Dipped and used wet.

B. Dipped, blotted, and used moist.

C. Dipped, dried in air, preserved over water.

D. Dipped, dried in air, preserved over calcium chloride.

E. Dipped, dried in an atmosphere of carbon dioxide, preserved over calcium chloride.

F. Dipped, dried in an atmosphere of carbon dioxide, preserved over water.

G. Dipped, dried in an atmosphere containing a large amount of ammonia, preserved over calcium chloride.

H. Dipped, dried in an atmosphere containing a large amount of ammonia, preserved over water.

The papers which were dipped and used without blotting (e. g., paper A) of course had a considerable amount of water adhering to them. They are designated as "wet," whereas those blotted before use (e. g., paper B) are termed "moist." This distinction between "wet" and "moist" is followed throughout this paper. The papers preserved in a desiccator over calcium chloride were, of course, thoroughly dry when used, while those kept over water contained enough moisture to be detected by touch. The difference in sensitivity of papers preserved over water and those preserved over calcium chloride is of importance as showing the possible variation of test results obtained when papers are kept under varying natural atmospheric conditions.

It is not an uncommon practice to prepare test papers and preserve them in contact with the air for some time before use, giving opportunity for absorption of carbon dioxide from the air by the lead salt in the paper. It was desirable, therefore, to determine what effect this might have on the sensibility of the papers. To accomplish this papers E and F were prepared.

It has been stated by a number of observers that exposing the test paper to ammonia vapor makes it more sensitive, but no conclusive experiments on this point had been reported. To test the truth of this contention papers G and H were prepared and used.

In the preparation of papers which are to be used dry, large sheets should be dipped in the lead acetate solution and then dried. The edges of these sheets should be trimmed off before cutting them up into the smaller test pieces. When the individual test papers are dipped and dried they are found to have a mottled appearance after exposure, the color appearing in irregular spots, particularly along the edges. Papers prepared by the first method give a more even distribution of the color.

The tests of these papers are illustrated in Fig. 5 and the details of the tests are given in Table 5. As in the previous set, the papers illustrated in the first row were exposed one-half minute, those of the second row one minute, and those of the third row three minutes. Papers prepared and used in the same manner appear in the same vertical column.

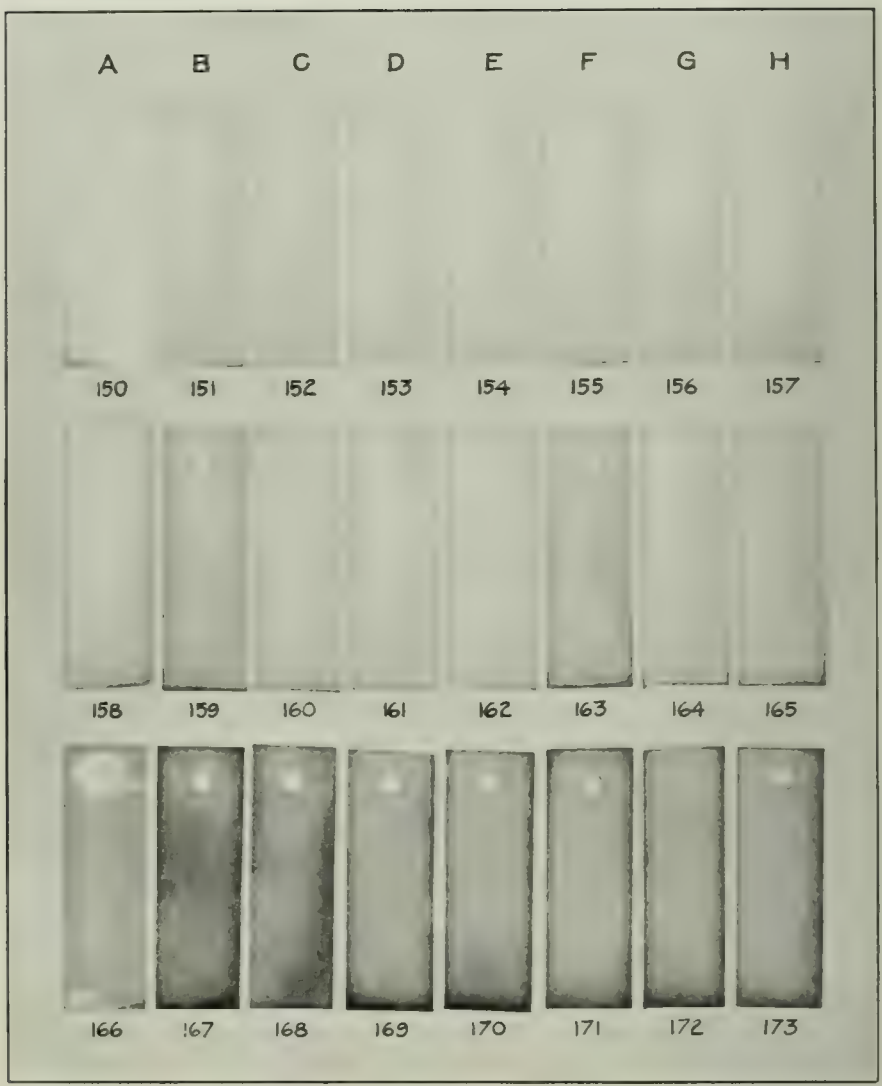

FIG. 5. *Effect of preparation and condition of test paper*

(Described in Table 5)

TABLE 5

Effect of Preparation and Condition of Test Paper

(Illustrated in Fig. 5)

[All tests were made in the standard apparatus, with gas containing approximately 1.1 grains hydrogen sulphide per 100 cubic feet.]

Test	Paper	Time	Color produced (standard color No.)	Remarks
150	A	0.5	4	Mottled.
151	B	0.5	3	
152	C	0.5	3+	
153	D	0.5	2−	
154	E	0.5	2+	
155	F	0.5	4	
156	G	0.5	2	
157	H	0.5	3—4	
158	A	1	5	Silvery appearance.
159	B	1	6−	
160	C	1	5	
161	D	1	4−	
162	E	1	4−	
163	F	1	8	
164	G	1	3—4	
165	H	1	5+	
166	A	3	8	Silvery.
167	B	3	8	Uniform color distribution.
168	C	3	7	
169	D	3	7+	
170	E	3	7	Darker than standard at edge.
171	F	3	7+	Black edges.
172	G	3	7	Black edges.
173	H	3	7	Dark edges, brown.

It is at once apparent that the moist papers are more sensitive than the dry papers. This will be discussed fully in a later section (see p. 24), where even a more striking example of the same effect is shown. The wet paper A, which is prepared by dipping and using without blotting, has an appearance very different from the other papers when it is exposed. It carries a surface film of lead acetate solution in which the hydrogen sulphide is precipitated, giving it a silvery appearance very unlike the other papers where the sulphide is precipitated on the paper fiber. This surface film, while wet, is easily removed by shaking or touching; and when dried it collects in patches and appears considerably lighter than when wet. Notice paper No. 166.

In comparing the moist papers B, C, F, and H, no decisive difference in their sensitivity was noted, at least none which might not be attributed to differences in individual test papers or unavoidable variations in the flow of gas over the test paper. Paper F, which had been dried in an atmosphere of carbon dioxide, seemed to be more sensitive in one or two tests than paper B; but this difference was not important and could not be definitely ascribed to the treatment with carbon dioxide.

No definite difference in sensitivity as compared with papers D and B was noted, either in this series or in a similar series, not illustrated, in the case of papers G and H, which had been treated with ammonia. Since there was no ammonia present on these papers when they were used, it was desired to test in another series the effect of free ammonia. To do this, papers, after being dipped and blotted, were held over concentrated ammonium hydroxide for one minute and then used at once. The coloration of papers so treated appeared to be somewhat lighter with gas of the strength used than the coloration of papers not exposed to the ammonia. These tests are illustrated in Fig. 6 and described in Table 6. Still other tests, not illustrated, were made on papers dipped in concentrated ammonium hydroxide solution, blotted, and used moist; these also showed a tendency to give less coloration, as compared with paper B.

TABLE 6

Effect of Ammonia on Sensitivity of Test Paper

(Illustrated in Fig. 6)

[All tests were made in the standard apparatus with gas containing approximately 1.1 grain hydrogen sulphide per 100 cubic feet.]

Test	Paper	Time (minutes)	Color produced (standard color No.)	Remarks
159A	H	1	6–	
174	B+NH_3	1	5–	Held one minute over concentrated NH_4OH.
175	B+NH_3	1	4–5	Held one minute over concentrated NH_4OH.

It is possible that the increase in sensitivity upon treatment with ammonia, which other authors have recorded, has been

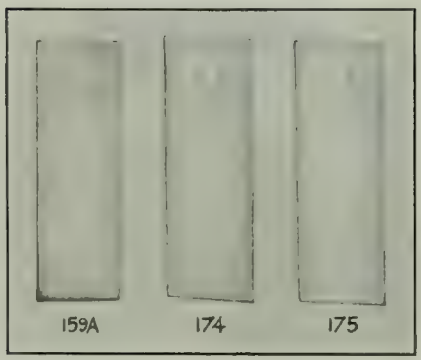

FIG. 6.—*Effect of ammonia on sensitivity of test paper*

(Described in Table 6)

really due to a comparison of dry paper with a paper which, during treatment with ammonia, had taken up considerable moisture. The increase in sensitivity which they noted should, therefore, probably be ascribed to moisture rather than to the ammonia.

4. SUMMARY AND RECOMMENDATIONS

An operator, giving consideration to the desired qualities noted above, can easily select the most suitable and convenient kind of paper after trying a number of samples, the convenience, but generally not the accuracy, of the test being affected by the choice.

There is little or no difference in the sensitiveness of paper prepared with lead acetate solution from 2 to 12 per cent in strength; a 5 per cent solution is recommended. Treatment of the papers with ammonia or carbon dioxide does not materially change their sensitiveness.

For reasons, some of which are given in the preceding section and others of which are made clear in the later discussions, the use of paper prepared in the same manner as paper B, i. e., dipped, blotted, and used moist, is recommended; such paper gives the most reliable and most nearly reproducible results.

VI. VARIATIONS DUE TO THE GAS

1. HUMIDITY OF THE GAS

The humidity of the gas and the condition of the paper, whether moist or dry, are factors which have a very decided influence on the sensitiveness of the test. This is strikingly shown by a series of tests on "dry" and "wet" gas with both moist (B) and dry (D) papers. In the first group of these tests the gas was dried after leaving the meter by passage through a tall calcium chloride tower (D of Fig. 1). When the tests on the dry gas had been completed, the connection to the drying tower was shut off and the gas, saturated at room temperature with water vapor by passage through the wet meter, was used directly.

The results obtained are tabulated in Table 7 and the test papers are shown in Fig. 7. The papers illustrated in the first horizontal row were used moist and the papers in the second row were

used dry. The first four vertical rows show tests made with dry gas and the second four with wet gas.

TABLE 7

Effect of Humidity of the Gas

(Illustrated in Fig. 7)

[All tests were made in the standard apparatus with gas containing approximately 0.7 grain hydrogen sulphide per 100 cubic feet.]

Dry gas				Wet gas			
Test	Paper	Time (minutes)	Color produced (standard color No.)	Test	Paper	Time (minutes)	Color produced (standard color No.)
67	B	0.5	4	75	B	0.5	3
69	B	1	4	77	B	1	4
71	B	3	6	79	B	3	7
73	B	5	6–7	81	B	5	8
68	D	0.5	1	76	D	0.5	2–
70	D	1	1–	78	D	1	3
72	D	3	1+	80	D	3	6
74	D	5	1+	82	D	5	7

It will be noted that the dry paper in the dry gas (Tests No. 68, 70, 72, and 74) gives only the faintest perceptible tinge even in five minutes, whereas the dry paper in the wet gas gave a distinct test in one-half minute (Test No. 76) showing the effect of the wet gas in moistening the paper. Practically the same test is obtained with moist paper when exposed for one-half or one minute in either the wet or dry gas; but when exposed for five minutes the strongest test is obtained with the wet gas, showing the drying effect of the dry gas. Although the moist paper exposed to the dry gas dries out very quickly and loses its sensitiveness, still it is more sensitive for short periods in the dry gas than the dry paper in the wet gas. On the other hand, when exposed for three to five minutes, the dry paper becomes sufficiently sensitive in the wet gas to give the same test as the moist paper exposed in the dry gas for the same length of time.

The use of dry test papers is not recommended, since the humidity of the gas may vary widely, being quite low whenever the gas has been subjected to low temperatures, thus making the

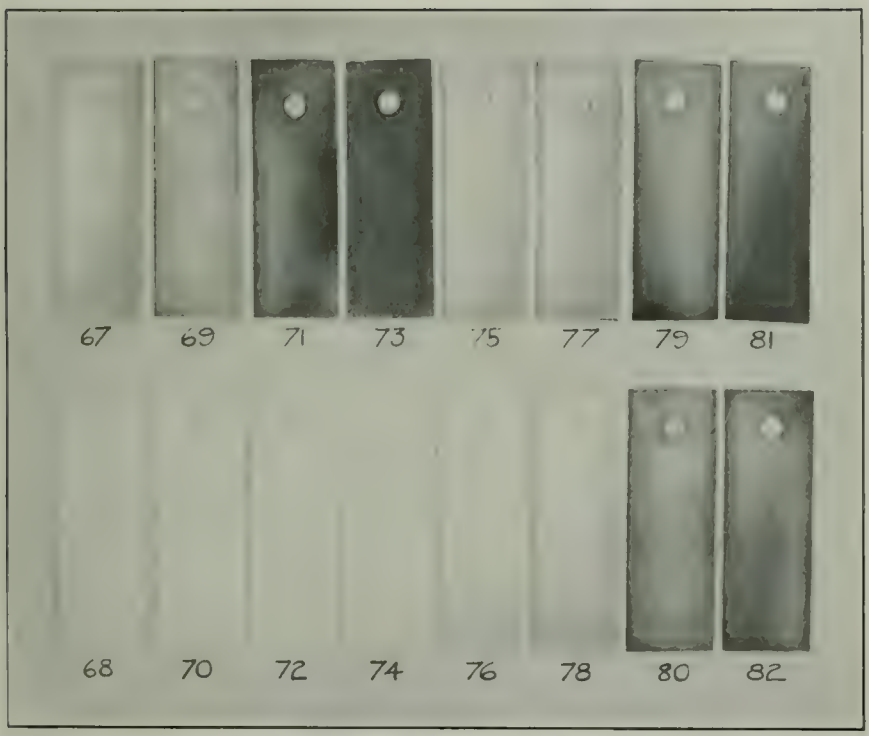

FIG. 7.—*Effect of humidity of the gas*

(Described in Table 7)

test variable and more dependent on the moisture content of the gas than on its hydrogen sulphide content. The moist paper is not "unduly sensitive" and it is evident that it will give the most reliable indications in practice.

2. RATE OF FLOW OF THE GAS

It is obvious that the depth of coloration obtained in any test depends not only upon the amount of hydrogen sulphide in the gas, but also upon the amount of the gas coming in contact with the paper. The time of exposure and the rate of flow of the gas will in part determine the amount of gas coming in contact with the paper. The effect, however, is not usually proportional to the quantity of gas passing; that is, the same test will not be obtained by exposing a paper for one minute to a gas flowing at the rate of 5 cubic feet per hour as by exposing the same paper to the same gas flowing at the rate of 1 cubic foot per hour for five minutes, although the same amount of gas flows through the apparatus in both cases. The coloration produced increases about proportionally with the increase in the time of exposure, but an increase in rate of flow gives much less than a proportional increase in coloration.

These effects of varying the rate of gas flow and the time are shown by the tests recorded in Table 8 and Fig. 8. When making tests at different rates, by-passes were so arranged that the apparatus under test and the by-pass in parallel with it at any time consumed a total of 5 cubic feet per hour, in order that the adjustment of the mixing apparatus would not be disturbed by changes in the rate of flow of the gas to the test apparatus. The by-passes were adjusted and calibrated in advance and were so arranged that a change in the gas rate could be made instantly. Comparisons could, therefore, be made quickly and without chance for variation in other conditions.

TABLE 8

Effect of Rate of Flow of Gas

(Illustrated in Fig. 8)

[All tests were made in the standard apparatus with gas containing approximately 0.5 grain hydrogen sulphide per 100 cubic feet.]

Test	Paper	Gas rate (cubic feet per hour)	Time (minutes)	Color produced (standard color No.)	Remarks
1	Blank	.....	.....	.....	
180	B	5.0	0.5	2–3	
181	B	5.0	1	3–4	
182	B	5.0	3	6	
189	B	3.5	0.5	2	
190	B	3.5	1	3–	
191	B	3.5	3	5	
192	B	0.8	0.5	1	
193	B	0.8	1	1+	
194	B	0.8	3	4–	
186	B	5.0	0.5	2+	Watch glass out (see p. 32).
187	B	5.0	1	3+	
188	B	5.0	3	6+	
181A	B	5.0	1	3–4	"Control" test (see p. 15).
195	B	.....	45	4–5	See p. 33.
196	B	5	3	1+	Referees apparatus.
183	D	5.0	0.5	1–2	Paper used dry.
184	D	5.0	1	2–3	
185	D	5.0	3	5–	

The lighter coloration produced at the lowest rate is quite apparent. The difference between the 3.5 and the 5.0 cubic feet per hour rates is not so noticeable; practically the same results would be obtained between the limits of 4.5 and 5.5 cubic feet per hour, and these limits were chosen for the method recommended.

3. TIME OF EXPOSURE

As pointed out in a previous paragraph, the time of exposure is very important in determining the depth of coloration produced, the sensitiveness of a test being roughly proportional to the time. However, attention may be called again to the tests made with dry paper in dry gas, where there was little difference noticeable between tests of one-half and five minutes' exposure. The proportionality above noted, however, holds good when the test paper is moist, unless a large amount of hydrogen sulphide is

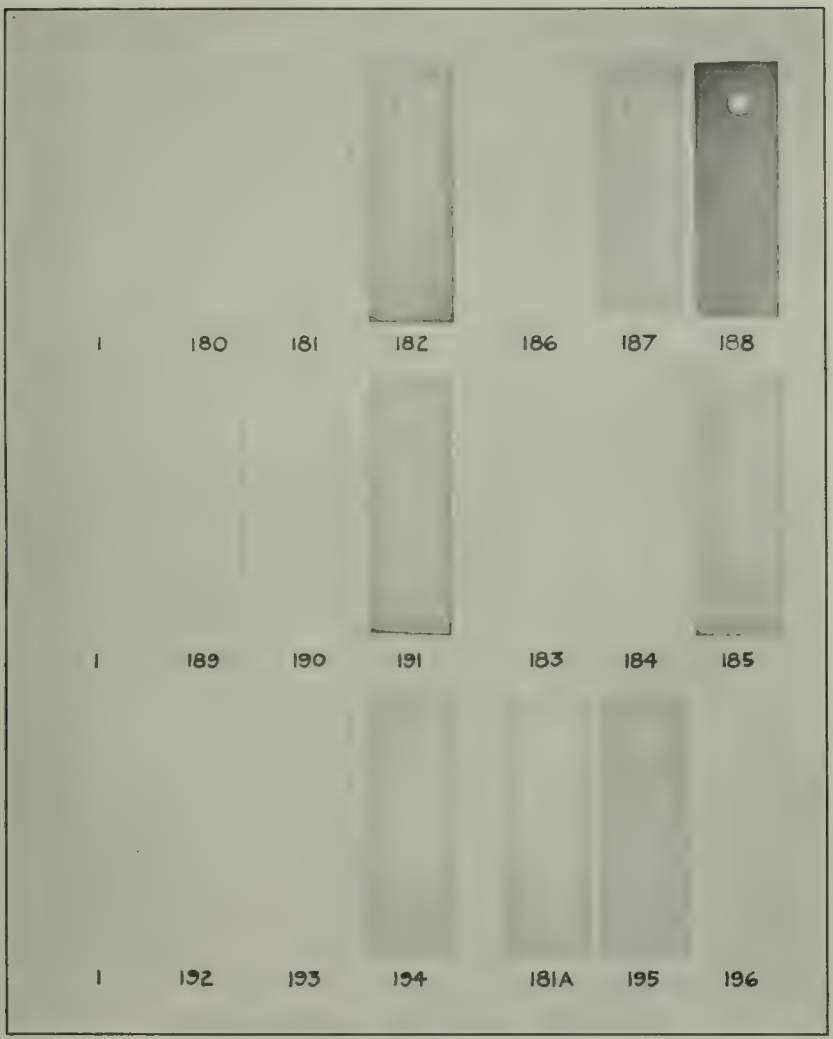

FIG. 8.—*Effect of rate of flow of gas*

(Described in Table 8)

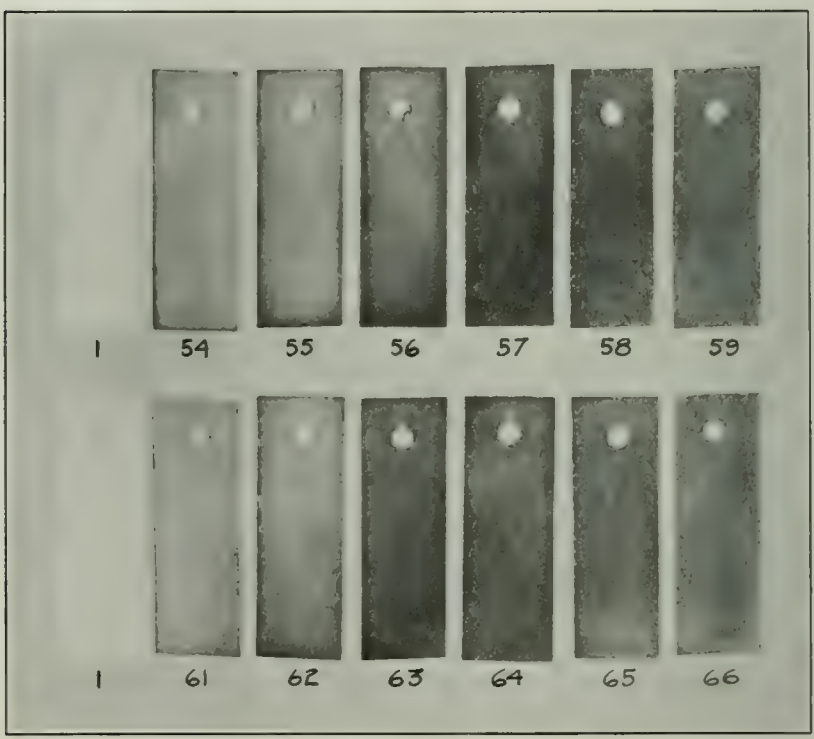

FIG. 9.—*Effect of time of exposure*

(Described in Table 9

present in the gas. In this latter case the depth of coloration does not increase so markedly with the time; this case is illustrated in the tests reported in Fig. 9 and Table 9. The papers exposed more than one minute show only slight increase in color, especially in the photographic reproductions, since the character of the coloration is changed slightly, becoming silvery. This is particularly true of the tests made with paper H, which had been treated with ammonia.

TABLE 9

Effect of Time of Exposure

(Illustrated in Fig. 9)

[All tests were made in the standard apparatus with gas containing approximately 2.7 grains hydrogen sulphide per 100 cubic feet.]

Test	Paper	Time (minutes)	Color produced (standard color No.)	Test	Paper	Time (minutes)	Color produced (standard color No.)
1	Blank	.....	.....	1	Blank	.....	
54	B	0.25	5	61	H	0.25	
55	B	0.5	6–7	62	H	0.5	Correspond closely to Nos. 54–59.
56	B	1	8	63	H	1	
57	B	2	8–9	64	H	2	
58	B	3	9	65	H	3	
59	B	4	9–10	66	H	4	

The variation in test results with time is illustrated in a majority of the other figures, and these should be noted in this connection.

4. SUMMARY AND RECOMMENDATIONS

The large effect of the humidity of the gas upon the test results is shown, but it is also noted that the use of moist paper with short test periods (not over three minutes) gives results practically independent of the humidity of the gas. It is impracticable either to dry or to saturate the gas to a constant condition as to humidity, because of the probability of simultaneous change in the hydrogen sulphide content.

The rate of gas flow is shown to have some effect, but increases in rate produce less effect than proportional increases in the time of test. The general practice of making tests at 5 cubic feet per hour is satisfactory; maintenance of the rate within the limits 4.5 and 5.5 cubic feet per hour is sufficient.

The time of test is an important factor in determining its sensitivity. The proper basis for selection of the length of test will be treated in connection with the discussion of the quantitative and engineering significance of the tests.

VII. FORMS OF TESTING APPARATUS

The different forms of testing apparatus used may be classified into three groups—circulating, impinging, and penetration—these being distinguished by the manner in which the gas is brought into contact with the paper. The five forms of circulating apparatus tested were: The simple hydrogen sulphide tester, chosen for this work and designated in this paper as the standard apparatus; the Referees apparatus; the Young's sulphur and ammonia test apparatus; the small drying-tower form; and a large Woulff bottle. Only one very simple form of the impinging type was tested; and a single penetration apparatus, devised by the authors, was used.

FIG. 10.—*Simple hydrogen sulphide tester, designated as "standard apparatus"* (½ *size*)

1. DESCRIPTION OF APPARATUS

(1) *Simple Hydrogen Sulphide Apparatus.*—The simple hydrogen sulphide tester, which is illustrated in Fig. 10, was devised in order to secure an apparatus which would be simple and inexpensive in form and such that it would permit rapid, easy, and accurately reproducible test results to be obtained. Although it follows other forms in many details, it has the advantage that it can be easily and cheaply made from materials obtainable in almost any chemical laboratory or drug store without the sacrifice of the advantages due to exactness of specifications.

This apparatus is made from a glass tube, or a common cylindrical gas chimney, 20 cm (8 inches) long and 4.5 cm (1.75 inches) in diameter, closed at top and bottom by perforated stoppers.

The pillar of a gas burner, from which the lava tip has been removed, is inserted through the lower stopper; and a small watch glass, 2.5–3 cm (1–1.5 inches) in diameter, is supported above the burner, to prevent the gas from impinging directly from the inlet on the test paper. The watch glass is supported on three glass pegs, 1–3 cm (0.4–1 inch) high, being held in place with small bits of wax. The gas is burned from an ordinary open-flame burner on the upper stopper; this burner should be so selected that it will pass 5 cubic feet of gas per hour under the ordinary pressure

FIG. 11*a*

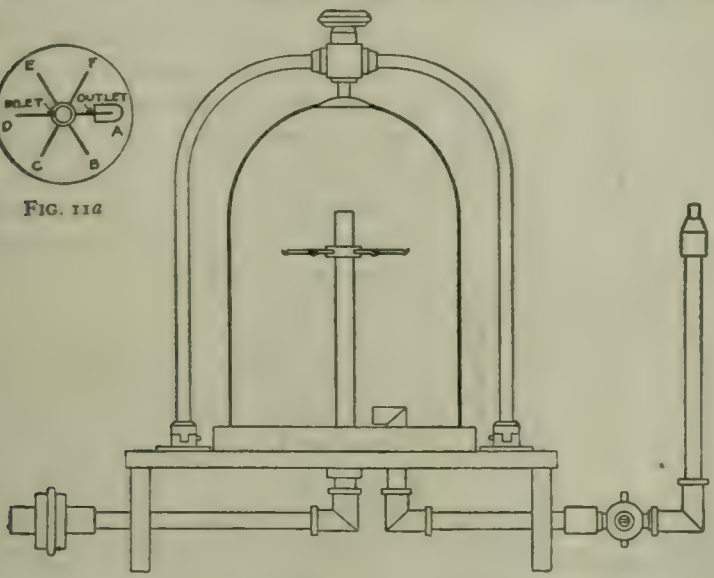

FIG. 11.—*Referees hydrogen sulphide test apparatus* (¼ *size*)

of the gas supply. The test paper, which should be 2 by 6 cm (0.75 by 2.4 inches), is hung on a glass hook so that it is held midway between the watch glass and the bottom of the upper stopper.

(2) *Referees Apparatus.*—This form (see Fig. 11) is one used commonly in this country and for all official testing in London and many other English cities. It consists essentially of a small bell jar held down into a mercury seal, arranged with a central inlet tube and outlet tube with elbow at the base. The test papers are hung on the six small hooks surrounding the inlet tube, as shown in the diagram, Fig. 11*a*.

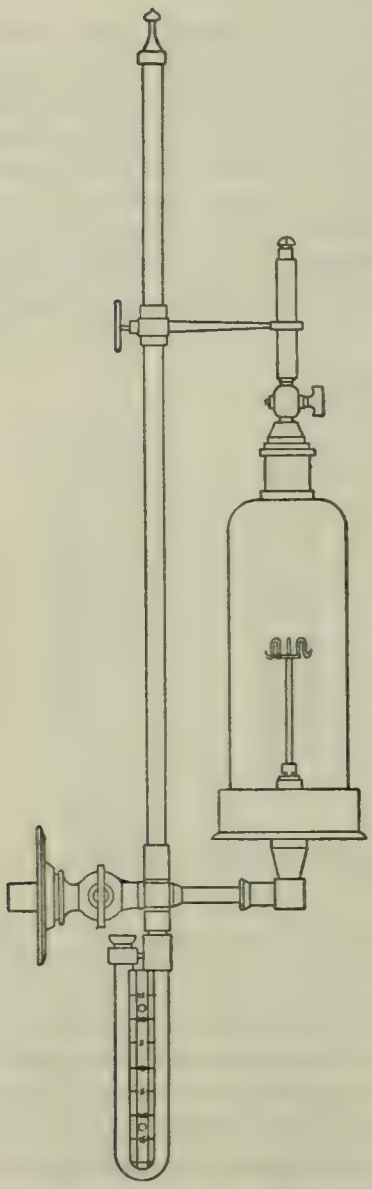

FIG. 12.—*Young's sulphur and ammonia test apparatus* (½ *size*)

(3) *Young's Sulphur and Ammonia Test Apparatus.*—In this form (see Fig. 12) the gas enters the test chamber through openings in the side of the pillar at the base and passes out through the cock and burner at the top. The small bell is taken off to insert or remove test papers by detaching the clamp from the upper pillar.

(4) *Small Drying-Tower Form.*—An ordinary calcium chloride tower (see Fig. 13) the upper chamber of which was about 14 cm (5.5 inches) long and 2.7 cm (1 inch) wide, inside diameter, was arranged by attaching an inlet tube at the base and a stopper with glass hook and burner at the top.

(5) *Large Woulff Bottle.*—This form was arranged as shown in Fig. 14, using a Woulff bottle 19 cm (7.5 inches) tall and 14 cm (5.5 inches) in diameter. The gas entered through the tube extending almost to the bottom and was burned at the burner on the right-hand stopper; test papers were hung on the glass hook in the central stopper. This apparatus was also used for a few tests in which the papers were exposed for 30 to 45 minutes to a sample of gas confined in but not flowing through the bottle.

(6) *Apparatus of Impinging Type.*—The only form of impinging apparatus tested consisted of a glass tube drawn out to a tip, from which the gas impinged directly upon the test papers held in

position at the desired distance in front of the jet. Some of the older forms of apparatus, similar in form to those of the circulating type, were so made that the gas issuing from small orifices impinged directly upon the test papers; the Referees apparatus used from 1877 to 1906 was of this form. None of these older forms of apparatus was tested.

(7) *Penetration Apparatus.*—The penetration apparatus used, which was devised by the authors, is shown in cross section in Fig. 15. The gas enters at the bottom, is forced through the test paper which is held between the two glass parts and is burned from the

FIG. 13.—*Small drying-tower form* (½ *size*)

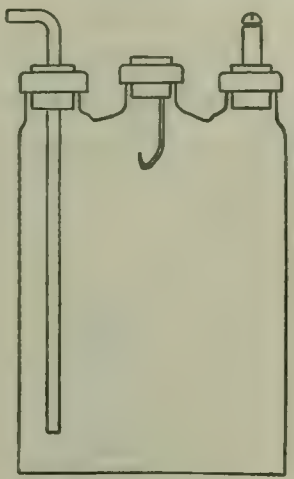

FIG. 14.—*Large Woulff bottle apparatus* (½ *size*)

FIG. 15.—*Penetration apparatus* (½ *size*)

burner at the top. The two halves of the apparatus are held together firmly by strong rubber bands between the glass hooks shown at the sides. The opening covered by the test paper is 1 inch in diameter; and the faces of the two sections are ground plane, so that there is a gas-tight connection when the rubber bands are in place. It was necessary to use only dry test papers in this apparatus, since moist paper is not sufficiently porous. The apparatus passed about 2.5 cubic feet of gas per hour and was used in parallel with a burner consuming the same amount, so that when substituted for other forms of apparatus it caused no change in the total gas rate.

2. COMPARISON OF APPARATUS

The results of a comparison of the five forms of circulating apparatus are given in Fig. 16 and Table 10. These tests show that the darkest coloration is produced in the small drying tower and the lightest in the Referees apparatus. Arranged in order of decreasing sensitiveness of test obtained, the forms of apparatus tested are as follows: (1) Small drying tower, (2) Young's sulphur and ammonia tester, (3) standard apparatus, (4) Woulff bottle, and (5) Referees apparatus. Another series of tests with dry paper showed the same results.

TABLE 10

Comparison of Apparatus

(Illustrated in Fig. 16)

[All tests were made with gas containing approximately 0.6 grain hydrogen sulphide per 100 cubic feet.]

Test	Paper	Time (minutes)	Apparatus	Color produced (standard color No.)
1	Blank			
101	B	0.5	Standard	1-2
102	B	0.5	Drying tower	3–
103	B	0.5	Woulff bottle	1+
104	B	0.5	Referees	1
105	B	0.5	Young's	2+
111	B	1	Standard	3
112	B	1	Drying tower	4
113	B	1	Woulff bottle	1–2
114	B	1	Referees	1
115	B	1	Young's	3
121	B	3	Standard	5
122	B	3	Drying tower	8–
123	B	3	Woulff bottle	4
124	B	3	Referees	1–2
125	B	3	Young's	6

Tests No. 186, 187, and 188, given in Fig. 8 and Table 8, show the effect of operating the standard apparatus without the usual watch glass above the inlet. By comparison with No. 180, 181, and 182, it will be noted that the coloration is slightly stronger when the watch glass is removed.

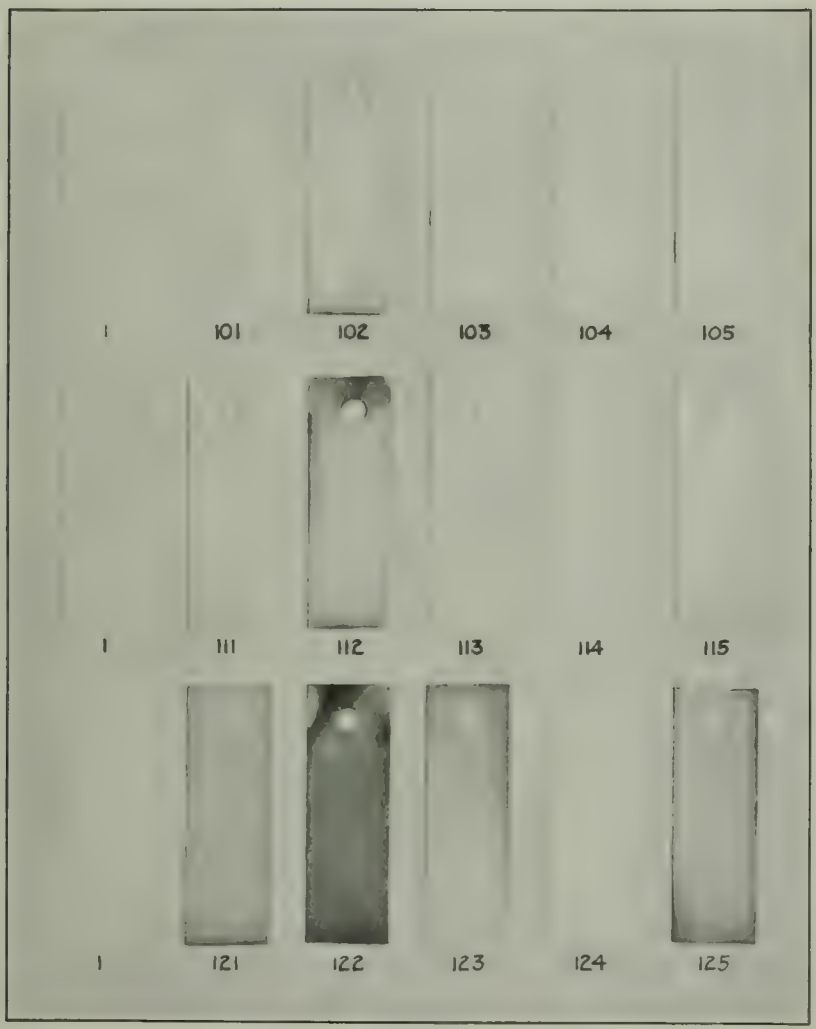

FIG. 10. *Comparison of apparatus*

Described in Table 12

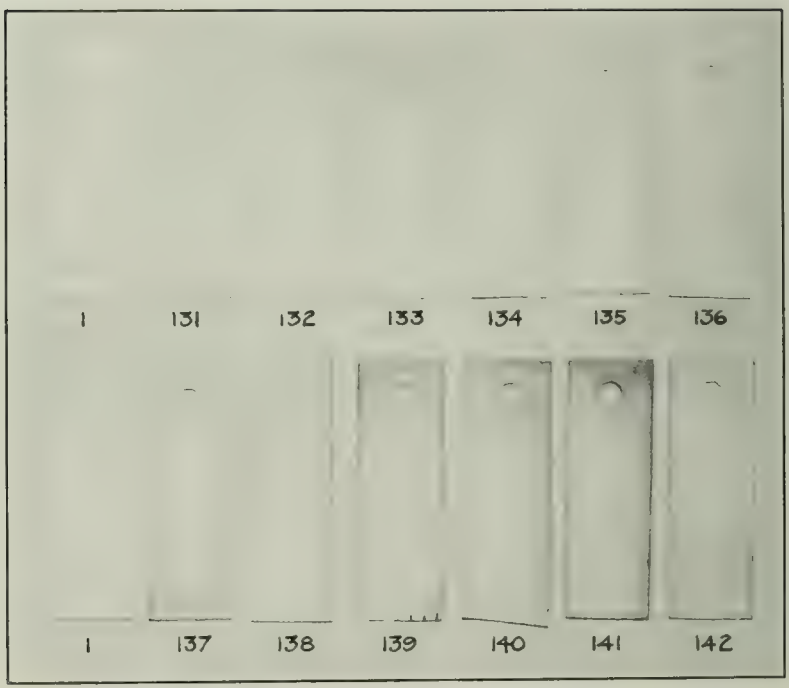

FIG. 17.—*Position of paper in Referees apparatus*

(Described in Table 11)

In the same table and figure is described a test, No. 195, in which a moist paper, B, was hung for 45 minutes in the Woulff bottle (Fig. 14) previously filled with gas containing 0.5 grain of hydrogen sulphide per 100 cubic feet.

The Referees apparatus is not symmetrical, the gas outlet being at the bottom near one side. A difference in the test obtained is noticed, depending upon which of the six hooks holds the test paper. The arrangement of these hooks with reference to the outlet is shown diagrammatically in Fig. 11*a*, the six possible positions for the test paper being lettered A to F. Two tests were made with a test paper suspended from each of the six hooks; the results are given in Fig. 17 and Table 11. In the three-minute test, shown in the upper row of the figure, the papers in positions A, B, and F show a very faint coloration; but the papers in positions C and E, and to a slightly less extent D, were more distinctly colored, particularly at their upper ends. The same differences are to be noted in the 10-minute test, the papers suspended in positions C, D, and E being darkest.

TABLE 11

Position of Paper in Referees Apparatus

(Illustrated in Fig. 17)

[Paper B was used in these tests, with gas containing approximately 0.6 grain of hydrogen sulphide per 100 cubic feet.]

Time, 3 minutes			Time, 10 minutes		
Test	Position of paper	Color produced (standard color No.)	Test	Position of paper	Color produced (standard color No.)
131		Blank	137		Blank.
132	A	1+	138	A	2+
133	B	1+	139	B	2
134	C	2	140	C	3
135	D	1–2	141	D	2–3
136	E	2	142	E	3
	F	1+		F	2

Only a few tests were made with apparatus of the impinging type; these showed very clearly the increase in sensitiveness when the gas was allowed to impinge on the paper from a jet. A moist paper, held 0.5 mm from the tip of a jet, from which the gas

issued at the rate of 1 cubic foot per hour, showed in half a minute a coloration that was just barely perceptible, but in one minute a distinct coloration was noted; whereas with the standard apparatus the same gas, at the rate of 5 cubic feet per hour, produced no coloration in five minutes. This gas contained approximately 0.1 grain hydrogen sulphide per 100 cubic feet (1 in 630 000 by volume). Increasing the rate of gas flow increased the sensitiveness of the test somewhat; and increasing the distance from jet to paper decreased the sensitiveness.

Since only apparatus of the circulating type is of importance in practical gas testing, very few tests were made on the other forms.

In Fig. 18 and Table 12 are given the results of one series of tests on the penetration apparatus. Tests with this apparatus are, of course, more sensitive than those made with any of the circulating type, since all of the gas is brought into intimate contact with the paper. The penetration apparatus may be useful when it is desired to have an extremely sensitive test, but for general inspection work it is not recommended.

TABLE 12

Tests with Penetration Apparatus

(Illustrated in Fig. 18)

[All tests were made with paper D and with gas containing approximately 0.6 grain hydrogen sulphide per 100 cubic feet flowing at 2.5–3.0 cubic feet per hour.]

Test	Time (minutes)	Color produced (standard color No.)	Remarks
144	1	5	Upper side of paper is shown, illustrating penetration of coloration through paper.
145	1	5	Lower side of paper is shown; lower side of 144 would match these.
146	1	5	
147	1	8	Lower and upper sides were about the same color.

3. SUMMARY

The variation in the tests with different forms of apparatus is largely due to the variation in intensity of the gas currents and their direction in relation to the paper. In the small drying tower the test paper was suspended close to the rubber stopper bearing the burner and a much larger proportion of the gas came in con-

FIG. 18. *-Tests with penetration apparatus*

(Described in Table 12)

tact with the paper than in the other forms of apparatus. Although the Woulff bottle had a larger capacity than the Referees apparatus, it consistently gave a stronger test than the latter, showing that size alone is not a determining factor; the shape of the apparatus and the location of the paper, relative to inlet and outlet, have an important influence.

In the case of the standard apparatus the removal of the watch glass was shown to make the test more sensitive (see p. 26), evidently because the flow of the gas over the surface of the paper is increased by this change. With the Referees apparatus a gas which was very near the limit might pass inspection when the paper was suspended from one hook and might be condemned when the test was made with the paper in a different position, again showing the variation in the results with differences in gas current over the test paper.

It has been generally recognized that a test in which the gas impinges on the paper is more sensitive than one in which the gas does not impinge. This is due to the better opportunity for contact of the gas with the reagent on the paper and to the smaller area within which the lead sulphide is concentrated. A similar increase in sensitiveness is accomplished by causing the gas to be tested to pass through the paper, as is done in the penetration apparatus described. This increase in sensitiveness, due to the impingement of gas on the paper, seems to have been overestimated by some, however. (See p. 43.)

The important influence of the shape and size of the apparatus upon the result of tests made with it makes clear the necessity of an exact specification of the form and size of the tester. It is therefore recommended that the specifications given for the apparatus which is used as standard in this work be followed exactly in making the tests.

VIII. QUANTITATIVE SIGNIFICANCE OF TEST

When the test is made under definite conditions, the coloration produced is of quantitative significance as indicating the amount of hydrogen sulphide present in the gas. The recognition of the amounts of hydrogen sulphide producing colorations of various intensities is a matter of experience and can not be adequately

described nor presented by photographs. However, the minimum amounts of hydrogen sulphide required to give a positive test under definite conditions can be quite closely approximated. Before discussing the sensitivity of the test, the methods used for the determination of hydrogen sulphide will be described.

1. DETERMINATION OF HYDROGEN SULPHIDE IN MIXTURES

Two methods were employed for determining the hydrogen sulphide content of the gas: First, calculation of the hydrogen sulphide content from the amount and concentration of the ether solution introduced; and, second, analysis of the gas by absorption of the hydrogen sulphide in a suitable medium and determination by titration with iodine. For the sake of brevity, the values secured by these two methods will be characterized as the "calculated" and the "analyzed" values, respectively.

The analysis of the solution of hydrogen sulphide in ether was carried out in the following manner: The tip of the weighed burette containing the solution was inserted into a small Erlenmeyer flask closed with a three-hole stopper. An inlet tube, through which hydrogen could be introduced, reached through a second hole halfway to the bottom of the flask; and an outlet tube in the third hole was sealed to the side tube of an Emmerling tower filled with glass beads so that all of the gas leaving the absorption flask had to bubble through this, in order to catch any hydrogen sulphide escaping absorption in the first flask. Ten cubic centimeters of a 5-per cent solution of cadmium acetate with 15 cc of dilute ammonium hydroxide was placed in the flask and about 30 cc of water with 5 cc of the ammonium hydroxide in the Emmerling tower. About 15 grams of the ether solution was run into the flask, slowly at first because of the rapid volatilization of the ether. The flask was then shaken intermittently for 5 to 10 minutes, while a slow stream of hydrogen was passed through the apparatus. The flask and the Emmerling tower were then washed out; and, after boiling off the ether and cooling the solution, hydrochloric acid was added and the liberated hydrogen sulphide titrated with N/100 iodine solution. The burette was weighed

again to obtain the exact weight of the sample taken and the hydrogen sulphide per gram of ether solution calculated.

In the analysis of the gas, the sample taken through the tube N (see Fig. 1) was bubbled through a neutral solution of cadmium acetate contained in a five-bulb absorption tube and then measured with a wet meter. The bulbs were washed out and the solution was heated to the boiling point to drive off any gases which might react with iodine. After diluting to 250 cc, 15 cc of 1:1 hydrochloric acid was added and 10 cc of N/100 iodine solution was run in; crystals of potassium iodide were added and the solution was titrated with N/100 sodium thiosulphate until the yellow color just disappeared. After the addition of 4 cc of fresh starch solution the titration was completed by adding more iodine solution until a pale blue tint appeared. The iodine required for the end point was determined by a blank test.

It should be noted that an ammoniacal or other alkaline solution can not be used without serious error in determining hydrogen sulphide in manufactured gas because of its action on other compounds than hydrogen sulphide. This fact has been overlooked by a number of writers who have used and recommended such solutions. Carbon disulphide reacts with ammonia and alkalies, forming compounds which liberate hydrogen sulphide upon acidifying. The following reactions among others, may take place:

$$CS_2 + 4NH_3 = NH_4CNS + (NH_4)_2S$$
$$3CS_2 + 6KOH = K_2CO_3 + 2K_2CS_3 + 3H_2O$$
$$K_2CS_3 + 2HCl = 2KCl + H_2S + CS_2$$

Absorption of hydrogen sulphide is probably incomplete in acid solution, but the permissible hydrogen ion concentrations have not been investigated. The use of an acetate solution would seem preferable to the use of a chloride solution, since the former can be kept practically neutral.

In order to give an idea of the relative quantities of ether, hydrogen sulphide, etc., employed in these procedures, the data obtained in the preparation of one gas mixture are given.

PREPARATION AND ANALYSIS OF GAS NO. 20

ANALYSIS OF ETHER SOLUTION OF HYDROGEN SULPHIDE

Weight of ether solution taken	15.75 gram	22.30 gram
Iodine solution consumed	3.13 cc	4.29 cc
Iodine solution equivalent to H_2S in 1 gram ether	.20 cc	.19 cc
Strength of iodine solution from standardization, 1 cc equals	0.000158 gram H_2S	
	or 0.00244 grain H_2S	
∴ 1 gram ether solution contained	0.0000308 gram H_2S	
	or 0.000476 grain H_2S	

CALCULATED STRENGTH OF GAS

Weight of ether solution taken	62.8 gram
Volume occupied by ether as vapor at 27° C and 759 mm (temperature and pressure in reservoir)	0.739 cu. ft.
Volume of gas taken	7.432 cu. ft.
Total volume of gas mixture	8.171 cu. ft.

$$\text{Hydrogen sulphide contained} = \frac{62.8 \times 0.000476 \times 100}{8.17}$$

$$= 0.37 \text{ grain } H_2S \text{ per 100 cu. ft.}$$

STRENGTH OF GAS DETERMINED BY ANALYSIS

Volume of gas taken for analysis	0.885 cu. ft.
Iodine solution used, corrected for thiosulphate used	1.59 cc
Hydrogen sulphide found (1.59×0.00244)	0.0039 grain
or (0.0039×100÷0.885)	0.44 grain per 100 cu. ft. of gas

RATE OF GAS FLOW

Total gas used	8.17 cu. ft.
Gas used for analysis	0.88 cu. ft.
Gas to testing apparatus	7.29 cu. ft.
Time of run	90 min.
Rate of gas flow to testing apparatus	4.85 cu. ft. per hour

Considerable difficulty was experienced in securing agreement between the calculated and analyzed values. The former were generally, as in the example cited, about 0.1 grain per 100 cubic feet lower than the analyzed values. This discrepancy, however, was not considered serious, since a difference of 0.1 grain per 100 cubic feet of gas (1 part in 630 000 by volume) makes no material difference in the interpretation of the results for commercial work. Moreover, the exact strength of the gas mixtures was of interest only in determining the quantitative significance of the tests; it has no bearing on the relative results reported in the

previous sections, nor on the discussion of the engineering significance in the later section.

In order to determine, if possible, why the analyzed values were almost invariably higher than the calculated values blank tests were made. In such a test a gas mixture, prepared by using ether which contained no hydrogen sulphide, was passed through the cadmium acetate solution in the usual way. After the usual length of run the solution was treated with iodine in the regular manner; only 0.06 cc of the iodine solution, practically a negligible amount, was required for the blank, showing that the method employed could scarcely be giving too high a result. Numerous other blank tests, made without adding ether to the gas, confirmed this conclusion. To detect any possible escape of hydrogen sulphide from the absorption apparatus, a test was made by passing a gas containing somewhat over 0.5 grain of hydrogen sulphide per 100 cubic feet through the absorption apparatus and then allowing it to impinge upon a moist lead acetate paper at the rate commonly used in analysis of the mixtures (0.6 cubic foot per hour) for 90 minutes. A copious precipitate of cadmium sulphide was obtained, but no stain was produced on the test paper. This shows that only very minute amounts of hydrogen sulphide could have been escaping from the absorber. The combined evidence of these several special tests gives good ground for confidence in the accuracy of the analyzed values.

The failure to get complete absorption of the hydrogen sulphide when adding the ether solution to the cadmium acetate solution was first suspected as the cause of low values for the calculated strength of the gas. However, increasing the time allowed for absorption was found generally to give still lower values, probably because of oxidation of sulphide, perhaps during the heating to expel the ether. Hydrogen was passed through the flask to minimize this oxidation.

These causes of uncertainty and the difficulties of exact sampling and titrating in the presence of ether made it seem probable that some error in the analysis of the ether solution of hydrogen sulphide was the cause of the discrepancy noted. However, to prove the point conclusively would have required an extended investigation

and much more time than the value of the results at this time would justify. The analyzed values were more concordant and were subject to no systematic error in so far as was known; they were, therefore, accepted in preference to the calculated values for use in the following section.

2. ABSOLUTE SENSITIVITY OF TESTS

In the determination of limiting sensitivity of any testing method which depends upon the appearance of a coloration, the personal judgment of the observer enters very largely. In the present case the test for hydrogen sulphide may have either of two objects: First, the detection of the smallest possible amount of this impurity; or, second, the determination as to whether or not a gas contains more than a permissible amount of the impurity. If a test were made in chemical work where the greatest sensitivity was desired, the first detectable coloration would be considered as sufficient to indicate the presence of hydrogen sulphide. However, in commercial work a distinct coloration would be required before hydrogen sulphide would be recorded as "present." The commercial application of this principle is explained more fully in the recommendations given later. In the following statements as to the sensitivity of tests, it is understood that a distinct coloration is required for positive results.

The results obtained in tests made on moist papers exposed for one minute in the standard form of apparatus are of greatest interest, since they represent the results obtained by the procedure which has been accepted as the standard for this work for reasons made clear in the section of recommendations.

From the various results obtained by this standard procedure, which are summarized in Table 13, it is evident that this test, if of one minute duration, would detect 0.5 grain of hydrogen sulphide per 100 cubic feet of gas; but with a gas of 0.25 grain no distinct test would be obtained. It is impossible to fix a limiting sensitivity of this test more specifically than to say that 0.3 to 0.4 grain of hydrogen sulphide per 100 cubic feet of gas is about the limit which would be detected. If the test is of one-half minute duration, it is of course less sensitive, about 0.45 grain of hydrogen sulphide being required to give a test; if it is extended

to three minutes, a gas of about 0.20 grain will give positive results. The variation in sensitivity, which would be produced by other changes in the test procedure, is evident from the numerous tables and figures given earlier in the paper.

It is not necessary to discuss more exactly the quantitative significance of the various combinations of conditions which are illustrated. It is of interest, however, to note again the relative sensitiveness of tests made with different forms of apparatus.

TABLE 13

Quantitative Significance of Tests

[Tests were made with moist paper (B) exposed for the period indicated in the standard apparatus with gas flowing at the rate of 5 cubic feet per hour.]

Test	Gas No.	Time (minutes)	Strength of gas (grains of H_2S per 100 cubic feet	Coloration produced (standard color No.)	Remarks
326	[illegible]	1	0.17	1	No coloration; would pass test.
315	[illegible]	1	.25	1	Coloration doubtful.
330	[illegible]	1	.30	1+	Very faint; might pass.
328	24	1	.32	1+	Slight color on bottom edge of paper; might pass.
[illegible]	20	1	.44	2	Would not pass test.
320	22	1	.47	2	Distinct; would not pass.
329	25	1	.72	2+	Very distinctly colored.
316	21	0.5	25	1	No coloration.
[illegible]	20	0.5	[illegible]	1+	Very faint.
322	22	0.5	.47	1+	Coloration doubtful.
327	23	3	17	1+	Very faint coloration.

The Young's apparatus is slightly more sensitive than the standard form; the Referees apparatus is much less sensitive, for it will scarcely detect 0.5 grain of hydrogen sulphide per 100 cubic feet of gas when used with moist paper for three minutes at a rate of 5 cubic feet of gas per hour. The sensitivity of a test with it varies also with the position of the paper, being greater for the positions on the side opposite the outlet tube.

The penetration apparatus is somewhat more sensitive than any of the forms of circulating apparatus. The sensitivity of the apparatus of the impinging type is variable, depending upon the rate of gas flow, distance of jet from paper, etc.; but under the most favorable conditions apparatus of this type is the most sensitive of all.

It was thought possible, though not probable, that the presence of the ether vapor in the gas mixtures might affect the sensitivity of the lead acetate papers. To determine whether or not such an effect was produced a gas mixture containing 0.45 grain hydrogen sulphide per 100 cubic feet was made with pentane instead of ether as the solvent for the hydrogen sulphide. This gas gave results which checked as closely as could be expected with a mixture of the same strength made with an ether solution. It was concluded, therefore, that the ether vapor in the gas had no effect beyond that produced by the hydrocarbons ("illuminants") already present in the gas.

3. COMPARISON WITH RESULTS OF PREVIOUS EXPERIMENTERS

The results obtained by Dibdin and Grimwood [7] apply only to tests made with the gas impinging from a jet upon the test papers; we have, therefore, only a small amount of data comparable with their results. It is quite certain, however, that somewhat too great a sensitivity has been ascribed to the procedures used by these experimenters. It should be noted that they do not give any information regarding the analytical method employed for the preparation or testing of the gas mixtures used and there are a number of points in their procedure which are open to criticism. In diluting the gas mixture to give a mixture of lower concentration, the residue of the previous mixture was flushed out with gas free from hydrogen sulphide and the reservoir was considered free from hydrogen sulphide when the gas escaping from it gave no test. In view of the fact that a rubber balloon which could easily absorb considerable amounts of hydrogen sulphide was hanging in the reservoir, it is doubtful whether a blank test made while the gas was passing through the apparatus would show conclusively that all hydrogen sulphide had been removed. When making up the more dilute mixtures, the rubber had opportunity to give off considerable amounts of hydrogen sulphide into the gas during the 30 to 45 minutes required for diffusion of the sample introduced. It is very probable that the gas mixtures which they obtained were, for this reason, richer in hydrogen sulphide than they

[7] Loc. cit.

believed. In any event, the evidence which they present is insufficient to show that this was not the case and it is necessary, therefore, to conclude that the results which they have presented are not conclusive as demonstrating the extreme sensitivity which they ascribe to the test. For example, instead of being able to detect 0.0006 grain hydrogen sulphide per 100 cubic feet of gas in a five-minute test, it seems certain that at least 0.01 grain, and probably more, of hydrogen sulphide per 100 cubic feet of gas would be required to give a coloration in a test of five minutes' duration; however, no attempt has been made in the present work to establish exactly the limiting sensitivity of the impingement method. It is desired, therefore, only to point out the probable fact that too great sensitivity has been ascribed in the past to the impingement tests.

The results given by Carpenter in the Alkali Works Inspector's Report[8] are also lacking in details as to the method of preparation and testing of the gas mixtures used. The sensitivity indicated for the mixtures containing from 0.6 to 0.006 grain of hydrogen sulphide per 100 cubic feet of gas is much less than that claimed by Dibdin and Grimwood. Our experience indicates that the conclusions expressed by Carpenter, though perhaps claiming too great sensitivity, are more nearly correct than those given by Dibdin and Grimwood.

The results which are reported by Ramsburg[9] do not indicate in every case all of the details which would be necessary to duplicate the tests exactly, but in so far as comparison has been made between the present work and that reported by Ramsburg very satisfactory agreement has been obtained. The sensitiveness indicated by him for the "present Referees method" is not very different from that which we have obtained; and the other tests indicate corresponding agreement. If any difference was to be noted, it would probably lie in indicating a greater sensitiveness for the tests as made by Ramsburg; but this slight difference could, we believe, be accounted for by the fact that he analyzed the gas mixtures used by a method, that of Hornby,[10] which tends to give

[8] Loc. cit [9] Loc. cit. [10] Gas Engineers' Laboratory Handbook.

results slightly too low because an acid absorbing solution is used. In other words, it is probable that a little more than 0.53 grain hydrogen sulphide per 100 cubic feet was present in the gas used by Ramsburg.

IX. TESTING PROCEDURE RECOMMENDED

In order to secure a test of exact reproducibility, it is desirable that detailed specifications should be observed both as to the form of apparatus and the testing procedure which are to be used. The apparatus recommended for use has been described on page 28 and is illustrated in Fig. 10. No variation from the specifications should be made without very careful consideration, for considerable care has been taken to prepare this apparatus in a form best suited for this work.

It should be noted that the test papers should hang as nearly as possible in the position indicated, namely, midway between the watch glass and the bottom of the upper stopper. If the papers are forced on, merely tearing them in order to put them in position, they will very often be suspended at an angle below the hook; the gas currents through the apparatus are then disturbed and normal results may not be obtained.

For each test the paper should be freshly prepared by submerging it in a 5-per cent solution of lead acetate and then pressing it between two sheets of blotting paper. It should then be hung in the apparatus and the test made at once, the time of exposure being regulated carefully. The gas should flow during test at between 4.5 and 5.5 cubic feet per hour. As soon as the test period is at an end, the flow of gas should be cut off and the test paper at once removed from the apparatus. If no distinct coloration is apparent, the paper should be compared with a similar strip of paper moistened with lead acetate in the same way as described above but not exposed to the gas. Hydrogen sulphide should be reported as present in the gas only when the test paper is *distinctly* darker than the paper not exposed to the gas. In case of uncertainty it is best in official testing work to report hydrogen sulphide as "absent." In other words, lack of conclusive evidence is sufficient to justify a negative report.

In making the test care should of course be taken to use gas fresh from the supply main and to insure that the gas before being tested does not come in contact with water, oil, or other substance by which the small amounts of hydrogen sulphide likely to be present in a commercial gas supply would be removed.

X. COMMERCIAL SIGNIFICANCE OF THE TEST PROPOSED

At the present time very different procedures are followed in testing for hydrogen sulphide and it is, therefore, impossible to say just how the tests which have been studied in the course of the present investigation compare with commercial testing methods in the majority of places. It is certain, however, that the standard procedure which is recommended above will give results which are less severe in their limitation upon a company than many of the tests now used; on the other hand, the procedure is slightly more severe than some of the test methods. particularly that known as the Referees method.

The time of exposure recommended (one minute) conforms to practice commonly found in this country and gives results probably of the desired commercial significance. A one-minute test requires very little time and yet is long enough to prevent any appreciable irregularity due to the unavoidable changes in time of exposure of the paper. Of course, if a more sensitive test is desired, a longer period can be used, or for a less severe test, a shorter period. If any change is made in the testing procedure in order to change the sensitiveness of the test, it is recommended that the period of the test be changed to accomplish this. In any case, the decision as to whether or not it would be desirable to make the test more or less stringent should be considered from an economic standpoint.

The object of the test should be to detect such amounts of hydrogen sulphide as are not commercially permissible, but it is difficult to determine just what limit should be chosen. It is certain that the testing method recommended is such that ordinarily careful operation of any common system of purification will give a gas sufficiently pure to meet the test. Therefore, in practically every case the test can be met without increasing the care now

exercised in the removal of hydrogen sulphide. Occasionally, of course, gas which will not pass the test must be sent out, but only the avoidable irregularities would cause any prolonged difficulty in meeting a test such as is proposed. It is assumed that the regulations under which the testing will be done will be drafted to care for the irregularities which can not be avoided, as suggested in Circular No. 32 of this Bureau. Many tests of similar severity, and some a great deal more severe, have been met regularly in the past, showing that the proposal is certainly not unreasonable.

XI. SUMMARY

The effect of the following variations in the method for the detection of hydrogen sulphide in gas with lead acetate paper has been investigated: (1) The kind of paper, its surface and opacity, method of preparation, strength of lead acetate solution used, and the moisture content of the paper when used; (2) variations due to changes in humidity of the gas, rate of gas flow, and time of exposure to gas; and (3) effect of the form and the size of the apparatus, which determine the gas currents in contact with the paper. A new apparatus and method are described for the continuous preparation of a uniform gas mixture containing a known amount of hydrogen sulphide. The results obtained show both the absolute and the relative sensitivity of the various methods which may be used in official or works laboratories; the quantitative as well as the commercial significance of the results is pointed out and comparisons are made with the results of previous observers. A method is recommended for use which is quick and convenient and gives reproducible results; and a simple and inexpensive form of apparatus is described which can easily be constructed by inexperienced persons without any sacrifice of the advantages due to exactness of specifications. The importance of conforming with the specifications, both as to the apparatus and the procedure in testing, is pointed out.

WASHINGTON, August 19, 1914.

DEPARTMENT OF COMMERCE

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STANDARDIZATION OF NO. 200 CEMENT SIEVES

BY

RUDOLPH J. WIG

and

J. C. PEARSON

[JULY 30, 1914]

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STANDARDIZATION OF NO. 200 CEMENT SIEVES

By Rudolph J. Wig and J. C. Pearson

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I. INTRODUCTION

The desirability of an improved standard for cement sieves has frequently been questioned on the ground that the fineness test, as ordinarily performed on the 200-mesh sieve, does not determine the quantity of the highly active material in the cement, and the results do not, therefore, necessarily give any indication of the quality of the cement. While this is probably true, it is obviously important from a commercial standpoint that cement furnished on contract according to specifications, and actually meeting the requirements for fineness, should not be rejected because an error has been made in the fineness determination, due to the use of inaccurate sieves or variation in the manipulation of the sieves. Such rejections, resulting in considerable financial loss, have been brought to the attention of the Bureau. The tolerance to be applied on the fineness determination should be such that it will cover all the unavoidable errors of the sieving tests. Experience has shown that the apparently liberal tolerance of 1 per cent previously suggested to cover the errors in fineness determinations on standard 200-mesh sieves, is not great enough, in very many cases, to cover the known variations in the sieves, and an improved standard seems, therefore, not only desirable but necessary.

The most important restrictions in the specifications for standard cement sieves are those which relate to the number of meshes per linear unit of the sieve cloth and to the diameter of the wire from which the cloth is woven. These sieve specifications serve as a guide to the wire cloth manufacturer but contain no reference to the performance of sieves as actually used in fineness determinations, the assumption being that the narrow limits of tolerance imposed would insure a satisfactory uniformity in sieving values.

Until recently no systematic investigation has been undertaken to check the uniformity of fineness determinations of standard sieves nor to establish the relation between measurements of the sieve cloth and the sieving values of these sieves. About two years ago the Bureau of Standards conducted such a series of tests [1] which established the fact that new certified standard

[1] Bureau of Standards, Technologic Paper, No. 29.

sieves differ very considerably in their sieving values, and that no specific relation could be found between the measurements of the sieve cloth and the observed sieving values. In view of this lack of uniformity a further investigation was undertaken, in the course of which it has been ascertained that some unsatisfactory sieves, from the user's point of view, have been certified as standard sieves, and many good ones, from the same point of view, have been rejected. This peculiar condition may be explained by the fact that the specifications for standard sieves, although permitting only the practical minimum of variations in number of meshes and wire diameters, do not limit the dimensions of the individual openings.

The specifications for standard sieves, issued by the Bureau in 1912,[2] contain the following requirements for 200-mesh sieves:

> Wire cloth for standard sieves for cement shall be woven (not twilled) from brass, bronze, or other suitable wire and mounted on frames without distortion. The sieve frames shall be circular, about 20 cm (7.87 inches) in diameter, 6 cm (2.36 inches) high, and provided with a pan about 5 cm (1.97 inches) deep and a cover.
>
> NO. 200 CEMENT SIEVE, 0.0029-INCH OPENING.
>
> The No. 200 sieve should have 200 wires per inch and shall conform to the following specification of diameter of wire and size of mesh:
>
> The diameter of the wires in the sieve should be 0.0021 inch and the average diameter of such wires as may be measured shall not be outside the limits 0.0019 to 0.0023 inch for either warp or shoot wires. The number of warp wires per whole inch, as measured at any point of the sieve, shall not be outside the limits 195 to 202 per inch and of the shoot wires 192 to 204 per inch. For any interval of 0.25 to 0.50 inch, in which the mesh may be measured, the mesh shall not be outside the limits 192 to 203 wires per inch for the warp wires and 190 to 205 wires per inch for the shoot wires.

It is evident from the foregoing that standard sieves may contain surprisingly large individual openings and still meet the specifications; and while users and manufacturers of sieves have known that all sieve openings are not uniform, they have perhaps failed to realize that a very large range in size of openings can exist under the specifications, and actually does exist in the best standard sieves. It is undoubtedly this variation in size of individual openings that contributes very largely to the differences in sieving values of standard sieves; and it is evident that the relatively large openings in particular must have an effect on

[2] Circular No. 39, Bureau of Standards.

the sieving value, which can not be calculated or even closely estimated from any readily applied system of averages.

It therefore appears that the specifications for standard sieves, which should be primarily for the benefit of the user, are not adequately serving their purpose, and it is felt that a revision thereof should now be made on the basis of the investigation reported herewith. The specifications have, however, improved the quality of sieves, as shown by tests of old and of new ones.

Opportunity is here taken to thank the many testing laboratories for their cooperation and to acknowledge the assistance of the weights and measures and the photometric divisions of the Bureau. Special acknowledgment is also due of the careful work done by Mr. W. H. Sligh and Mr. D. W. Kessler in connection with the sieving tests.

II. SCOPE OF INVESTIGATION

This paper discusses the results of a number of observations made to determine methods of standardizing the 200-mesh sieve and its manipulation, so that greater uniformity may be obtained in its use. In the course of the investigation a study has been made of the following:

1. The accuracy of sieving tests, personal equation in sieving, variations in sieving values of standard sieves, and precautions necessary in sieving tests.

2. The results of sieving tests made in 85 different laboratories and a comparison of these results with those obtained by the Bureau of Standards on some of the same sieves.

3. Four proposed methods of standardizing sieves.

4. The suitability of a number of finely ground materials, as compared with Portland cement, for use in calibrating sieves.

5. The adoption of a standard value of fineness.

6. The application of a "correction" to the sieving value of standard sieves.

7. A revised specification for standard sieves.

III. SIEVING TESTS v. SIEVE MEASUREMENTS AS A BASIS OF CERTIFICATION FOR STANDARD SIEVES

1. UNIFORMITY OF RESULTS OF SIEVING TESTS AND PERSONAL EQUATION IN SIEVING

A choice between methods of standardizing cement sieves should be made on the basis of suitability and accuracy. The purpose of this discussion is to show that on the basis of accuracy, that is, on the basis of uniformity in the results which are being sought, sieving tests are preferable to microscopic calibration of the sieve cloth as a method of standardization.

In determining the sieving values of about 75 standard sieves with a specially prepared sample of cement, a maximum range in these values has been verified of slightly more than 4 per cent. A larger range has been found in the results of similar tests made in other laboratories, and it is probably safe to assume that certified standard sieves may vary 5 per cent in their sieving values.

The general accuracy of the sieving tests which have made up the greater part of this investigation is shown in Table 1. This table contains the variations from the average sieving values in 40 fineness determinations obtained by three operators, each making independent tests with samples of carefully mixed cement. In all these tests conditions were directly comparable, and all the results are tabulated. It is the practice of the Bureau in making these determinations to compare the three independent results thus obtained and to consider these satisfactory if the range is not appreciably greater than 0.5 per cent. If the range is greater than this amount, a retest is made by the operator whose result is most at variance with the others, and sometimes two or even three retests are made. All results obtained on any one sieve, however, are averaged in determining the sieving value of that sieve.

The results presented in Table 1 show that a single fineness determination by a competent operator should not be more than 0.5 per cent in error and is generally much closer than this, as indicated by the average variations of 0.12, 0.15, and 0.16 per cent, respectively.

TABLE 1

[Showing the Percentage Variations of Three Operators and the Range of Values obtained in 40 Fineness Determinations; 23 different Sieves were Used in these Tests]

Test No.	P	S	K	Range	Test No.	P	S	K	Range
1	+0.11	−0.19	+0.07	0.30	24	+ .01	− .07	+ .05	.12
2	− .10	+ .30	− .20	.50	25	+ .01	+ .15	− .15	.30
3	− .01	+ .21	− .19	.40	26	+ .01	− .07	+ .07	.14
4	− .23	+ .03	+ .21	.44	27	+ .11	− .25	+ .13	.38
5	− .20	+ .16	+ .04	.36	28	− .07	− .15	+ .21	.36
6	− .01	− .11	+ .13	.24	29	+ .20	− .38	− .18	.70
7	− .03	+ .01	+ .01	.04		+ .32	+ .04		
8	+ .13	− .13	− .01	.26	30	+ .02	− .36	+ .38	.74
9	− .13	+ .05	+ .07	.20			− .04		
10	+ .03	− .21	+ .17	.38	31	− .09	− .11	+ .19	.30
11	+ .16	− .32	+ .30	.62	32	− .04	− .20	+ .24	.44
		− .16			33	− .10	− .12	+ .22	.34
12	+ .03	− .15	+ .11	.26	34	− .11	− .15	+ .27	.42
13	− .02	+ .06	− .04	.10	35	− .01	− .19	+ .21	.40
14	− .34	− .06	+ .34	.68	36	+ .17	− .03	− .13	.30
			+ .04		37	+ .12	− .16	+ .04	.28
15	− .05	− .01	+ .05	.10	38	− .01	− .11	+ .13	.24
16	− .46	+ .04	+ .16	.92	39	+ .16	− .28	+ .12	.44
	− .22		+ .46		40	+ .16	− .26	+ .10	.42
17	− .16	+ .18	− .02	.34					
18	− .30	− .04	+ .30	.60	Highest	+ .32	+ .30	+ .46	.92
			+ .04		Lowest	− .46	− .38	− .20	.04
19	− .06	− .20	+ .26	.46	Algebraic average	− .03	− .10	+ .12	
20	− .04	− .20	+ .24	.44					
21	− .01	− .19	+ .21	.40	Average, disregarding sign	.12	.15	.16	.38
22	− .32	− .26	+ .28	.60					
			+ .28						
23	− .05	− .17	+ .21	.38					

The algebraic average of each operator's variations shows his tendency to get higher or lower results than the others, and to this extent it represents his "personal" equation in sieving. These "personal equations" are remarkably small, in view of the fact that each of the three operators has developed well-defined peculiarities in sieving.

It is evident, therefore, that carefully made sieving tests of themselves involve far less uncertainty in the performance of a sieve than mere certification according to the present specifications. It is conceivable, however, that a very poor screen may have its imperfections so distributed that a fairly good sieving value will be obtained in tests similar to those described above but the graduation of the material passing through would not be comparable with that passing a uniformly woven screen. Such

a sieve should be rejected irrespective of its sieving value, and in general it may be stated that satisfactory sieving tests without any other restriction whatever are not sufficient grounds for certification.

2. PRECAUTIONS NECESSARY IN SIEVING TESTS

It will be shown later that much larger variations in sieving values are reported from other laboratories than those given in Table 1. Therefore, it should be emphasized that a dependable sieving test requires care and patience on the part of the operator as well as strict attention to certain essential details of the operation.

The standard specifications for sieving [3] are as follows:

> The determination of fineness should be made on a 50-gram sample, which may be dried at a temperature of 100° C (212° F) prior to sifting. The coarsely screened sample (cement is ordinarily screened through a No. 20 sieve before mixing for routine test) should be weighed and placed on the No. 200 sieve, which, with the pan and cover attached, should be held in one hand in a slightly inclined position and moved forward and backward in the plane of inclination, at the same time striking the side gently about 200 times per minute against the palm of the other hand on the upstroke. The operation is to be continued until not more than 0.05 gram will pass through in one minute.

It is not necessary, however, that the entire sieving test be performed in this way, and a slight modification has been found to give more uniform results and to be far less fatiguing to the operator. The operation, as now carried out and recommended by the Bureau of Standards, is as follows:

Place the 50-gram sample on the 200 sieve with pan attached. Holding sieve and pan (without the cover) in both hands, sieve with a gentle wrist motion until most of the fine material has passed through, and the residue looks fairly clean. This operation usually requires only three or four minutes. Should there be any small lumps of fine material remaining, mash them up very gently against the screen with the ball of the forefinger, being careful to remove none of the coarser particles in this process.

When the residue appears clean, place the cover on the sieve, remove from pan, and, holding sieve and cover firmly in one hand, tap the side of the sieve gently with the handle of the brush used for cleaning the sieve (a three-fourths inch bristle brush with

[3] United States Government Specification for Portland Cement, Circular 33, Bureau of Standards.

a 10-inch handle is a convenient size). Dust adhering to the sieve will thus be dislodged, and the underside of the screen may then be swept clean. Empty the pan and wipe out thoroughly with a cloth or waste. Replace the sieve in the pan and remove the cover carefully. If any of the coarser material has been caught in the cover during the tapping, see that it all gets back into the sieve.

The sieving may now be continued as before (with the cover removed) for 5 or 10 minutes, depending on the condition of the cement. The gentle wrist motion involves no danger of spilling the residue, the latter being kept well spread out on the screen, and the sieving is thus going forward much more easily and rapidly than when the specifications are followed throughout. More or less continuous rotation of the sieve is desirable throughout the operation. This open sieving may usually be continued safely for eight minutes or more, but care should be taken that it is not continued too long.

The cover should then be replaced and exactly the same process of cleaning followed as before. If the cement is in proper condition, there should now be no appreciable dust remaining in the residue nor adhering to sieve or pan.

The one-minute tests should now be made strictly according to specifications. It has been found, however, that 150 strokes per minute are equally as effective as 200 per minute and easier for the operator. Regular rotation of the sieve is essential, and the practice of sieving about 25 strokes in 10 seconds by the watch, then turning the sieve 60° and sieving for another 10 seconds, and so on throughout the one-minute tests, is conducive to uniform results. Sieves having covers with handles can be turned about the right amount without any trouble whatever, and flat covers may be marked with three straight lines through the center and intersecting at 60°. If one of the lines is marked with an arrowhead, and the habit is formed of starting this point under the right hand, one can easily keep track of the progress of the one-minute test. In the one-minute tests the sieve should be tapped rather than struck, for a gentle vibration of the screen is all that is required. Any considerable blow on the sieve will throw the residue against the cover and very likely result in the loss of material.

The essential points in the standard sieving operation may be summarized as follows:

1. Rotation of the sieve throughout the process, and particularly in the one-minute tests.

2. Guarding against loss of material. Most sieves are provided with covers which do not fit closely and are otherwise poorly made. If loss is suspected, sieve over white paper and always tap the sieve gently.

3. A good balance which may be relied upon to 1 or 2 milligrams is required. The ordinary cement laboratory balance, exposed to dust and rough usage, is not accurate enough for this work.

4. Washers, shot, and slugs should not be used on the sieve except in routine work—never in check tests nor in standardizing tests.

5. Avoid important tests on damp days. Excessive humidity interferes with good sieving. It tends to decrease the percentage of cement passing the sieve and, in general, to produce irregular results.

It has been suggested that the labor of making the sieve test might be considerably reduced by stopping the sieving when not more than 0.1 gram passes the sieve in one minute. While the difference in apparent fineness by this method as compared with present practice must be considerable, the relative uniformity obtained in the abbreviated method may not be inferior to that now obtained. Sufficient work has not been done to determine this, but it is being further investigated.

The use of a machine for making sieving tests has been advocated by many on the ground that a properly designed mechanical shaker should give more uniform results than can be obtained in hand sieving. It has been observed, however, that while a given machine may yield consistent results, different machines will give different results, sometimes considerably at variance with those obtained by hand. Therefore, however excellent may be the action of any one machine, unless this machine be universally adopted as a standard, it must eventually be checked by hand sieving. Difficulties also arise in connection with cleaning the sieves and making the one-minute tests; and it is doubtful if a machine can be very advantageously employed in standardizing work unless the number of sieves to be tested is large.

IV. COOPERATIVE SIEVING TESTS

1. VARIATION IN SIEVING VALUES OF STANDARD SIEVES AS DETERMINED BY THE BUREAU OF STANDARDS AND OTHER LABORATORIES

Under date of January 28, 1914, a circular letter was sent to practically all the cement-testing laboratories in the United States, requesting those who possessed 200-mesh sieves which had previously been certified by the Bureau of Standards to cooperate in determining the sieving values of these sieves on standard samples of cement furnished by the Bureau. The purpose of these tests was, first, to establish a definite standard of fineness and, second, to determine the approximate "corrections" to sieves based on this standard. A sufficient amount of cement was sent to the owners of the certified sieves for three tests on each sieve. Those participating in the investigation were asked to submit individual results of the tests, in order that the uniformity which was being obtained might be compared with that obtained by the Bureau.

Following is a list of the laboratories participating in the cooperative investigation:

Allentown Testing Laboratory, Allentown, Pa.
Alpha Portland Cement Co., Easton, Pa.
American Bureau of Inspection and Tests, Chicago, Ill.
Armour Institute of Technology, Chicago, Ill.
Ash Grove Lime & Portland Cement Co., Kansas City, Mo.
Atlas Portland Cement Co., Northampton, Pa.
Atchison, Topeka & Santa Fe Ry., Topeka, Kans.
Baltimore & Ohio R. R. Co., Baltimore, Md.
Bureau of Standards, Washington, D. C.; Pittsburgh, Pa.; Northampton, Pa.
California Portland Cement Co., Colton, Cal.
Cape Girardeau Cement Co., Cape Girardeau, Mo.
Chicago, Milwaukee & St. Paul R. R. Co., Chicago, Ill.
Chicago Portland Cement Co., Oglesby, Ill.
Colorado Portland Cement Co., Denver, Colo.
Coplay Portland Cement Co., Coplay, Pa.
Crescent Portland Cement Co., Wampum, Pa.
Dewey Portland Cement Co., Dewey, Okla.
Dexter Portland Cement Co., Nazareth, Pa.
District of Columbia Testing Laboratory, Washington, D. C.
Dixie Portland Cement Co., Richard City, Tenn.
Eastern Testing Laboratories, Allentown, Pa.
Erie R. R. Co., Jersey City, N. J.
Fredonia Portland Cement Co., Fredonia, Kans.
German-American Portland Cement Co., La Salle, Ill.
Glens Falls Portland Cement Co., Glens Falls, N. Y.

Giant Portland Cement Co., Philadelphia, Pa.
Gulick-Henderson Co., Pittsburgh, Pa.
Hunt Co., Robt. W., Chicago, Ill.; Pittsburgh, Pa.; New York, N. Y.; St. Louis, Mo.; Seattle, Wash.; San Francisco, Cal.; Los Angeles, Cal.; Vancouver, British Columbia.
Huron Portland Cement Co., Alpena, Mich.
Inland Portland Cement Co., Metaline Falls, Wash.
Iola Portland Cement Co., Iola, Kans.
Iowa Portland Cement Co., Des Moines, Iowa.
Iowa State College, Ames, Iowa.
Michigan Portland Cement Co., Chelsea, Mich.
Millen Co., Thos., Jamesville, N. Y.
New Castle Portland Cement Co., New Castle, Pa.
New York Public Service Commission, New York, N. Y.
New York State Commission of Highways, Albany, N. Y.
New York State Engineering Department, Albany, N. Y.
Odgen Portland Cement Co., Brigham City, Utah.
Oklahoma Portland Cement Co., Ada, Okla.
Olympic Portland Cement Co., Bellingham, Wash.
Penn-Allen Portland Cement Co., Nazareth, Pa.
Pennsylvania Cement Co., Nazareth, Pa.
Pittsburgh Testing Laboratory, Pittsburgh, Pa.; Easton, Pa.; Dallas, Tex.
Riverside Portland Cement Co., Riverside, Cal.
Sandusky Portland Cement Co., Sandusky, Ohio.
Santa Cruz Portland Cement Co., Davenport, Cal.
Smith Emery & Co., San Francisco, Cal.
Southern States Portland Cement Co., Rockmart, Ga.
Southwestern States Portland Cement Co., El Paso, Tex.
Standard Portland Cement Co., Leeds, Ala.
Three Forks Portland Cement Co., Trident, Mont.
Tidewater Portland Cement Co., Union Bridge, Md.
Union Portland Cement Co., Devils Slide, Utah.
Union Sand & Materials Co., St. Louis, Mo.
United States Engineer Office, Cincinnati, Ohio.
United States Reclamation Service, Denver, Colo.; San Francisco, Cal.; Elephant Butte, N. Mex.
Universal Portland Cement Co., Chicago, Ill.
University of California, Berkeley, Cal.
University of Wisconsin, Madison, Wis.
Vulcanite Portland Cement Co., Philadelphia, Pa.
Washington Filtration Plant, Washington, D. C.
Washington Portland Cement Co., Concrete, Wash.
Western States Portland Cement Co., Independence, Kans.
Wolverine Portland Cement Co., Quincy, Mich.
Wyandotte Portland Cement Co., Wyandotte, Mich.

Of the 254 standard 200-mesh sieves which had been certified by the Bureau up to July 1, 1914, 162 were tested with the stand-

ard sample of cement; 16 others were located, but the results of the tests were not received. The results obtained are given in Tables 2 and 3.

TABLE 2

Results of Sieving Tests Made by Various Laboratories on a Standard Sample of Cement Furnished by the Bureau of Standards

[a=1 determination, b=2 determinations, c=4 determinations, d=5 determinations, e=6 determinations. No. 716 was dried below 250° F.]

Sieve marked B. S. No.—	Per cent passing 200 mesh	Range of three or more determinations	Variation from standard value of 77 per cent	Sieve marked B. S. No.—	Per cent passing 200 mesh	Range of three or more determinations	Variation from standard value of 77 per cent
4	76.50	0.62	−0.50	241	78.58	0.06	+1.58
5	76.45	.30	− .55	318	77.20	1.30	+ .20
6	76.68	.50	− .32	320	77.70	.28	+ .70
7	76.65	.40	− .35	332	78.65	.10	+1.65
9	77.47	.40	+ .47	345	79.02	.05	+2.02
10	76.67	.10	− .33	346	86.60	.40	+9.60
11	77.83	.20	+ .83	346	76.70b	.20b	− .30
12	77.21	.40	+ .21	365	76.47	.60	− .53
13	78.20a	.....	+1.20	371	78.07	.20	+1.07
14	77.55	.82	+ .55	372	79.80	.40	+2.80
16	77.19	.09	+ .19	373	78.93	.20	+1.93
46	79.55	1.07	+2.55	374	79.23	.10	+2.23
46	79.55	.41	+2.55	375	79.11	1.04	+2.11
47	77.80a	.....	+ .80	375	79.01	.10	+2.01
48	79.33	.10	+2.33	382	76.23	.08	− .77
49	78.07	.10	+1.07	408	79.53	.38	+2.53
51	78.00a	.....	+1.00	409	78.50a	.....	+1.50
52	76.80a	.....	− .20	410	80.07b	.04b	+3.07
52	77.00a	.....	.00	411	77.69	.25	+ .69
53	77.00a	.....	.00	415	77.75	.12	+ .75
53	76.80a	.....	− .20	416	77.43	.78	+ .43
54	77.00a	.....	.00	416	77.47	.13	+ .47
54	77.00a	.....	.00	418	77.47	.20	+ .47
66	79.71c	.03c	+2.71	419	76.93	.10	− .07
67	77.37	.50	+ .37	427	77.87	.10	+ .87
67	77.10	1.00	+ .10	429	77.53	.20	+ .53
68	76.06	.33	− .94	430	79.08b	.04b	+2.08
69	78.60b	.00b	+1.60	431	76.93	.20	− .07
75	78.70c	.70c	+1.70	432	78.00	.00	+1.00
76	77.57	.21	+ .57	433	73.80a	.....	−3.20
[illegible]	77.09	.25	+ .09	434	76.49	1.08	− .51
80	76.44a	.....	− .56	434	76.84	.25	− .16
142	77.84	.46	+ .84	435	78.45	.18	+1.45
145	76.84	.44	− .16	436	76.07	.10	− .93
146	76.83	.40	− .17	437	74.77	.52	−2.23

TABLE 2—Continued

Results of Sieving Tests Made by Various Laboratories on a Standard Sample of Cement Furnished by the Bureau of Standards—Continued

[a=1 determination, b=2 determinations, c=4 determinations, d=5 determinations, e=6 determinations. No. 716 was dried below 250° F.]

Sieve marked B. S. No.—	Per cent passing 200 mesh	Range of three or more determinations	Variation from standard value of 77 per cent	Sieve marked B. S. No.—	Per cent passing 200 mesh	Range of three or more determinations	Variation from standard value of 77 per cent
438	76.93	0.40	—0.07	623	78.14	1.04	+1.14
439	75.87	.20	—1.13	624	77.24	.20	+ .24
440	77.83	.30	+ .83	627	77.54	.48	+ .54
441	77.67	.30	+ .67	676	77.73	.02	+ .73
471	78.57	.78	+1.57	678	78.43	.30	+1.43
472	79.39c	.12c	+2.39	679	76.83	.30	— .17
474	78.67	.20	+1.67	680	79.37	.14	+2.37
475	78.58	.16	+1.58	685	79.48b	.28b	+2.48
476	78.26	1.41	+1.26	686	76.47	1.00	— .53
480	78.72	.22	+1.72	687	78.85	.06	+1.85
493	80.60	.00	+3.60	690	78.24	.12	+1.24
493	77.80	.40	+ .80	691	77.27	.80	+ .27
496	77.86b	.07b	+ .86	692	77.20	.20	+ .20
498	76.90b	.20b	— .10	694	77.22	.36	+ .22
499	76.54a	.....	— .46	695	76.68	.38	— .32
499	77.79	1.14	+ .79	709	79.58b	.08b	+2.58
529	76.27	.20	— .73	710	78.54	.10	+1.54
530	77.67	1.20	+ .67	712	78.66	.18	+1.66
576	76.41d	.42d	— .59	713	80.00a	.....	+3.00
587	78.72	.23	+1.72	714	78.41	.46	+1.41
589	75.33	.20	—1.67	714	78.54	.18	+1.54
590	75.07	.40	—1.93	715	76.90	.40	— .10
591	73.60a	.....	—3.40	716	75.44	.39	—1.56
592	76.57	.10	— .43	720	77.03	.10	+ .03
593	76.20b	.30b	— .80	721	77.17	.30	+ .17
611	75.87	.20	—1.13	722	76.23	.30	— .77
615	77.36	.82	+ .36	723	77.13	.20	+ .13
615	77.35	.15	+ .35	730	77.47	.36	+ .47
616	78.53a	.....	+1.53	731	78.73	.10	+1.73
616	75.95	.25	—1.05	732	77.53	.10	+ .53
617	79.00a	.....	+2.00	733	76.44b	.35b	— .56
617	75.59	.30	—1.41	734	77.68	.42b	+ .68
619	77.80b	.00b	+ .80	737	77.40a	.....	+ .40
620	77.03	.10	+ .03	739	77.00a	.....	.00
622	76.36	.36	— .64	739	77.20a	.....	+ .20

The results reported in Table 2 were obtained by the laboratories owning the sieves. The results show a range of not more than 1

per cent for three or more determinations in any one laboratory, excepting in eight cases. The maximum variation from the finally adopted standard of 77 per cent for all laboratories was 9.60 per cent, but retests in a number of cases indicated that practically all determinations showing a variation of more than 3 per cent from the standard were unreliable. Thus retests on sieves Nos. 346, 433, 437, 493, 590, and 591 showed that the first results obtained on these sieves were considerably in error. Disregarding these results, the highest value reported is 80.07 per cent on sieve No. 410, and the lowest is 75.33 per cent on sieve No. 589, showing a maximum range of 4.74 per cent.

The results reported in Table 3 are from tests that have been made at the Bureau on 38 new sieves submitted by the manufacturers for certification. The total range of sieving values obtained is only 1.44 per cent and testifies to a decided improvement in manufacture of the more recent sieves.

TABLE 3

Results of Sieving Tests Made at the Bureau of Standards on the Standard Sample of Cement Furnished to Other Laboratories

[c=4 determinations, d=5 determinations, e=6 determinations.]

Sieve marked B. S. No—	Per cent passing 200 sieve	Range of three determinations	Variation from standard value of 77 per cent	Sieve marked B. S. No—	Per cent passing 200 sieve	Range of three determinations	Variation from standard value of 77 per cent
70	77.12	0.04	+0.12	93	78.29d	0.66d	+1.29
71	77.94	.24	+ .94	94	77.49	.42	+ .49
72	77.25	.10	+ .25	121	77.73	.22	+ .73
73	77.61	.22	+ .61	122	78.03	.12	+1.03
74	77.94	.28	+ .94	124	77.27	.16	+ .27
77	77.24	.10	+ .24	125	77.65d	1.00d	+ .65
79	77.09d	.70d	+ .09	126	77.41d	.64d	+ .41
81	77.72d	.70d	+ .72	127	78.23	.30	+1.23
82	77.76d	.90d	+ .76	128	77.35	.40	+ .35
83	78.11	.72	+1.11	129	76.91c	.64c	— .09
84	78.23	.26	+1.23	130	77.33	.52	+ .33
85	77.49	.46	+ .49	132	78.35	.46	+1.35
86	77.76e	.52e	+ .76	133	77.72c	.62c	+ .72
87	78.30	.26	+1.30	134	76.97	.40	— .03
88	78.25	.22	+1.25	136	77.56c	.62c	+ .56
89	77.36c	.62c	+ .36	137	77.30c	.68c	+ .30
90	77.17d	.58d	+ .17	138	77.75	.10	+ .75
91	77.75c	.54c	+ .75	139	77.68	.34	+ .68
92	77.97	.50	+ .97	140	77.32c	.60c	+ .32

2. COMPARISON OF SIEVING VALUES OBTAINED BY THE BUREAU OF STANDARDS AND OTHER LABORATORIES ON THE SAME SIEVES

In a number of cases the results reported in Table 2 showed unexpected variations, and an endeavor was therefore made to get as many comparisons as possible between results obtained on the same sieves in the Bureau and in other laboratories. A number of privately owned sieves were submitted for this purpose on request, and a number of others were purchased after tests had been made by the Bureau and were subsequently retested by the owner.

Table 4 contains the results of sieving tests made by the Bureau and other laboratories on the same sieves. The last column shows that in about one-half of the cases where check determinations were made differences of over 1 per cent were obtained. These variations would be rather discouraging were it not for the fact that several of them were obtained from check tests on questionable determinations, and there is no reason to believe that the average discrepancy between the Bureau's results and those of other laboratories is nearly as large as the average of those in Table 4. Nevertheless, these comparisons show that considerable errors may occur when the sieving tests are made carelessly or without due regard to all directions. Since in very many cases it is not possible to know whether the tests have been properly made, it has not been deemed advisable to base a standard on the results obtained from the cooperative tests. The reasons for the adoption of a value of 77 per cent as the fineness of the standard sample submitted are given in a later paragraph, but it may be pointed out that the approximate "corrections" to the tested sieves (which are obviously the values given in the last column of Table 2 with the opposite sign) are approximate only to the degree of excellence of the sieving tests on which they are based. Each operator must decide for himself whether his personal error is sufficient to affect the reliability of the "correction factor" which he has determined by his tests.

TABLE 4

Comparison of Results of Sieving Tests Made by the Bureau of Standards and Various Laboratories on a Standard Sample of Cement Furnished by the Bureau of Standards

Sieve marked No.	Bureau of Standards	Outside laboratories	Variation from Bureau of Standards determinations	Sieve marked No.	Bureau of Standards	Outside laboratories	Variation from Bureau of Standards determinations
51	77.93	78.00	+0.07	80	77.62	76.44	—1.18
66	79.03	79.71	+ .68	433	77.93	73.80	—4.13
	79.11		+ .60	437	76.57	74.77	—1.80
67	78.63	77.37	—1.26	499	76.75	76.54	— .21
		77.10	—1.53			77.79	+1.04
68	76.86	76.06	— .80	590	75.69	75.07	— .62
69	77.33	78.60	+1.27	591	75.51	73.60	—1.91
75	77.45	78.70	+1.25	623	77.79	78.14	+ .35
76	78.61	77.57	—1.04	624	76.95	77.24	+ .29
78	77.32	77.09	— .23	710	78.35	78.54	+ .19

V. A COMPARISON OF METHODS OF TESTING SIEVES

Since the real purpose of standardizing cement sieves is to insure their correctness and uniformity, the criterion for any method of standardizing is the reliability with which the results may be interpreted in terms of sieving values. This discussion is devoted to a comparison of results of three methods which have been used or which have been proposed for testing sieves.

1. RELATION BETWEEN SIEVE MEASUREMENTS AND SIEVING VALUES AND VARIATIONS IN SIEVE OPENINGS

The present method of certification of a sieve consists in determining (1) the average diameter of the wires, (2) the average number of meshes per linear inch, (3) the maximum and minimum number of meshes per whole inch interval, and (4) the maximum and minimum number of meshes per quarter-inch interval.

The maximum variations which are permitted in sieves which meet the specifications are given on page 5.

Table 5 contains the data taken from the certificates of 43 standard sieves, together with their sieving values as determined in the Bureau's laboratory on the cement used in the cooperative

tests. The most obvious relation between the observed sieving values and the other measurements appears to be in the wire diameters—that is, the smaller the wires the more open the sieves. Thus, sieves 67 and 84 have the smallest average wire diameters and high sieving values, while sieves 4, 6, 437, 499, and 591 have the largest average wire diameters and low sieving values.

It might be presumed that the most uniform sieves would be those which come nearest to the ideal sieves as indicated by the certification measurements; for example, let us select those sieves of which the average wire diameters are not outside the limits 0.00205 inch to 0.00215 inch, the average meshes per linear inch are not outside the limits 199 to 201 and the average meshes in quarter-inch intervals for either warp or shoot are not outside the limits 196 to 204. (These limits are about as close as it is possible to have them and not exclude all the sieves; thus, if the quarter-inch limits were made 197 and 203, no sieve in this list would meet these requirements.) The parentheses indicate the sieves which are within these limits. It is seen that the sieving values of these selected sieves range from 76.36 per cent to 78.30 per cent, and while this may be considered quite satisfactory, there are no less than 23 of the presumably inferior sieves which have sieving values also within these limits. Moreover, the average sieving value of the 15 selected sieves is 77.48 per cent, while that of the other 23 is 77.35 per cent; that is, a better average sieving value than that of the selected sieves. Without attempting to further analyze the data in Table 5, it is quite evident that the certification measurements as made heretofore do not justify a very reliable deduction as to sieving values, and indicate only a general tendency toward openness or closeness in the sieves. The data show, however, that as the sieves are now being made, the dimensions are for the most part well within the tolerances of the bureau specifications, and that the average wire diameter and mesh of the sieves is usually very close to the nominal values .0021 inch and 200 meshes per inch, respectively.

As already stated in the introduction, it is believed that the variation in sieving values of sieves is due largely to the variations in the individual openings. That these openings are quite irregular in all grades of 200-mesh sieves is shown in Table 6.

TABLE 5

Results of Measurements and Relative Sieving Values of 200-Mesh Standard Sieves

Sieve No.	Average diameter of wires, ten-thousandths inch		Average number of meshes per linear inch		Range in number of wires per linear inch								Fineness of standard sample as determined by sieving test	Variation from standard value of 77 per cent
					In whole-inch intervals				In quarter-inch intervals					
					Warp wires		Shoot wires		Warp wires		Shoot wires			
	Warp	Shoot	Warp	Shoot	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.		
4	23	22	200	197	199	200	193	204	197	202	190	205	76.50	− 0.50
5	22	22	200	197	199	200	194	198	196	203	192	200	76.45	− .55
6	23	22	200	195	199	200	193	196	198	203	192	198	76.68	− .32
7	22	22	200	197	200	200	194	200	196	202	193	204	76.65	− .35
51	20	20	199	197	198	202	196	198	196	203	196	198	77.93	+ .93
66	20	20	198	194	197	199	193	195	196	202	192	197	79.11	+ 2.11
67	19	20	198	199	198	199	196	203	196	200	195	204	78.63	+ 1.63
(68)	(21)	(22)	(200)	(201)	(199)	(201)	(199)	(203)	(198)	(202)	(198)	(204)	(76.86)	−(0.14)
(69)	(21)	(22)	(200)	(200)	(199)	(201)	(197)	(202)	(196)	(203)	(196)	(204)	(77.33)	+(0.33)
70	22	22	199	201	197	200	199	202	196	202	198	205	77.12	+ .12
(71)	(21)	(21)	(199)	(199)	(198)	(200)	(198)	(200)	(196)	(201)	(197)	(203)	(77.94)	+(0.94)
72	22	22	200	200	198	201	198	202	197	203	196	203	77.25	+ .25
73	22	22	200	200	199	200	196	202	196	203	191	204	77.61	+ .61
(74)	(22)	(21)	(201)	(199)	(199)	(202)	(198)	(201)	(198)	(202)	(196)	(202)	(77.94)	+(0.94)
75	22	22	199	200	197	201	199	202	196	203	197	202	77.45	+ .45
76	20	20	198	198	198	199	197	200	196	200	195	201	78.61	+ 1.61
77	22	22	201	200	200	202	198	202	197	203	197	204	77.24	+ .24
(78)	(21)	(21)	(201)	(201)	(199)	(202)	(199)	(203)	(197)	(203)	(198)	(204)	(77.32)	+(0.32)
(79)	(21)	(21)	(200)	(200)	(199)	(202)	(197)	(202)	(197)	(203)	(196)	(204)	(77.09)	+(0.09)
80	22	21	199	200	197	200	195	202	196	202	192	204	77.62	+ .62
(81)	(22)	(21)	(201)	(200)	(199)	(202)	(198)	(202)	(198)	(203)	(196)	(204)	(77.72)	+(0.72)
(82)	(22)	(20)	(199)	(200)	(198)	(201)	(197)	(201)	(196)	(202)	(196)	(202)	(77.76)	+(0.76)

83	22	20	200	199	198	201	196	201	194	203	194	202	78.11	+ 1.11
84	20	19	197	190	196	198	196	203	196	198	194	205	78.23	+ 1.23
(85)	(22)	(21)	(200)	(199)	(199)	(201)	(197)	(201)	(197)	(202)	(196)	(203)	(77.49)	+(0.49)
86	22	21	201	200	199	202	197	202	197	203	195	204	77.76	+ .76
(87)	(22)	(21)	(199)	(199)	(198)	(200)	(197)	(201)	(196)	(203)	(196)	(202)	(78.30)	+(1.30)
88	22	19	201	199	200	202	196	200	197	203	194	202	78.25	+ 1.25
89	21	20	200	200	199	201	197	201	197	203	195	203	77.36	+ .36
(90)	(22)	(21)	(200)	(200)	(199)	(200)	(198)	(202)	(197)	(202)	(196)	(203)	(77.17)	+(0.17)
(91)	(21)	(20)	(199)	(200)	(198)	(200)	(198)	(201)	(196)	(203)	(196)	(203)	(77.75)	+(0.75)
92	21	20	201	199	200	202	196	201	196	203	193	203	77.97	+ .97
(93)	(21)	(20)	(199)	(199)	(198)	(201)	(197)	(201)	(197)	(203)	(196)	(202)	(78.29)	+(1.29)
94	21	20	200	200	200	201	196	203	197	202	195	204	77.49	+ .49
433	22	22	198	199	197	200	196	201	195	202	195	204	77.93	+ .93
437	23	22	200	197	200	201	195	199	197	203	194	201	76.57	− .43
499	23	22	200	201	199	201	200	203	196	203	198	204	76.75	− .25
576	22	22	200	199	199	200	197	202	197	200	194	203	76.41	− .59
591	23	22	198	196	196	200	194	197	194	202	192	200	75.51	− 1.49
(622)	(21)	(21)	(199)	(200)	(199)	(200)	(197)	(202)	(196)	(202)	(196)	(204)	(76.36)	−(0.64)
623	21	20	199	197	198	201	194	201	195	204	192	202	77.79	+ .79
(624)	(20)	(21)	(199)	(200)	(198)	(200)	(198)	(202)	(196)	(202)	(196)	(204)	(76.95)	−(0.05)
710	21	21	198	200	198	199	198	203	196	201	197	204	78.35	+ 1.35

This table shows the variations in size of two sets of 10 consecutive openings in both warp and shoot wires as measured on four sieves of widely varying sieving values. The places selected for measurement were not necessarily the worst places on the sieves, but were taken where the variation was seen to be considerable after a brief inspection under the microscope.

The results on these four sieves serve as another illustration of the inadequacy of the present specifications, for according to this method of certification sieves 294 and X fail to meet the requirements, whereas 576 and 66 now bear the Bureau of Standards seal. Sieving tests would indicate that 576 and X are the better sieves.

The most striking conclusion that may be drawn from the measurements recorded in Table 6 is that the warp wires are spaced very much more irregularly than the shoot wires. In fact, the microscope is not needed to show up the imperfections of the warp, as the latter can always be distinguished by the naked eye, by simply holding the sieve up to the light and noting the bands of light and shadow produced by the unevenness in the spacing of the warp wires, whereas the shoot wires appear more uniform and are without distinct bands. Over an interval as large as a quarter inch, however, which is the minimum interval considered in the specifications, the *average* mesh of the warp wires is usually nearer the nominal mesh of 200 per inch than is that of the shoot wires. Just why the individual openings of the shoot wires should be invariably more uniform than those of the warp is not plain, when it is remembered that the latter are spaced mechanically while the former are driven in by hand. This irregularity in spacing of the warp wires should be subject to improvement by the manufacturer, but we are not able at the present time to suggest a reasonable modification of the specification which will improve the cloth in this respect.

Figs. 1 and 2 show some of the imperfections and irregular spacing of the wires in two of the best standard sieves in the Bureau laboratory. The broken and loose wires are, of course, only local defects, whereas the irregular spacing extends across the sieve. The magnification in these photographs is such that if the entire sieve were shown on the same scale, it would cover a circular area 30 feet or more in diameter.

TABLE 6

Comparison of Measured Openings and Sieving Values of Four 200-Mesh Sieves

Sieve marked—	No.	Openings between warp wires (inch)		Openings between shoot wires (inch)		Warp openings		Shoot openings		Sieving value
						Maximum	Minimum	Maximum	Minimum	
	1	0.0024	0.0032	0.0029	0.0027					
	2	26	33	28	29					
	3	31	30	30	31					
	4	49	33	25	29					
	5	26	28	30	30					
294	6	28	34	39	28	0.0049	0.0024	0.0039	0.0025	74.5
	7	29	26	38	29					
	8	28	24	26	33					
	9	25	34	29	27					
	10	24	24	25	29					
	1	.0034	.0029	.0031	.0025					
	2	39	24	29	30					
	3	28	25	29	29					
	4	27	36	30	31					
	5	25	26	28	29					
576	6	23	25	28	30	.0041	.0019	.0031	.0025	76.4
	7	36	26	28	26					
	8	27	24	27	30					
	9	31	41	27	28					
	10	25	19	29	29					
	1	.0042	.0030	.0032	.0030					
	2	29	28	31	31					
	3	29	41	31	32					
	4	20	25	27	32					
	5	32	25	31	32					
X	6	33	27	32	33	.0044	.0020	.0036	.0027	77.5
	7	30	30	29	29					
	8	30	24	27	27					
	9	29	23	28	29					
	10	44	35	31	36					
	1	.0029	.0026	.0027	.0030					
	2	36	51	29	30					
	3	26	25	27	29					
	4	30	24	29	34					
	5	32	32	31	30					
66	6	22	30	38	30	.0051	.0022	.0039	.0027	79.1
	7	25	24	39	31					
	8	38	23	32	29					
	9	24	38	28	30					
	10	24	34	29	29					

In this connection it is interesting to refer to an article by G. J. Griesenauer [4] on "A Sieve Test for Cement that Insures Uniformity in Fineness." In this paper the author called attention to the fact that by holding a sieve in such manner that the cement always passed back and forth across the warp wires, a higher percentage passing the sieve was invariably obtained than when the test was made by sieving across the shoot wires. A number of tests were made at the Bureau of Standards which in a general way confirmed Mr. Griesenauer's results, although the differences observed were less, and no greater uniformity was obtained than in the usual method of rotating the sieve. The invariable lack of uniformity in the spacing of the warp, however, suggests the explanation for a higher sieving value across the warp wires, for it is evident that if the cement is moving in the lengthwise direction of the large openings the particles are more likely to pass through these openings than when moving across them. Furthermore the greater bending of the warp wires produces in effect a rougher surface across the warp than across the shoot, and the particles are thus "pocketed" in this direction more readily than when moving across the shoot.

The tests performed by Mr. Griesenauer are therefore additional evidence that the variations in sieving values are closely related to the imperfections in the spacing of the warp wires.

2. A PROPOSED OPTICAL TEST OF SIEVES AND ITS RELATION TO THE SIEVING VALUES

Inability to interpret the usual certification measurements of sieves in terms of sieving values led to a search for some method of standardization, from the results of which might be drawn a satisfactory inference with regard to sieving values, thus avoiding the very considerable labor of making the actual sieving tests. Unfortunately the optical method proposed and tried out was found to be inadequate, but a brief description of the test is here given.

[4] A sieve test for cement that insures uniformity in fineness, Engineering News, 70, p. 1296, Dec. 25, 1913.

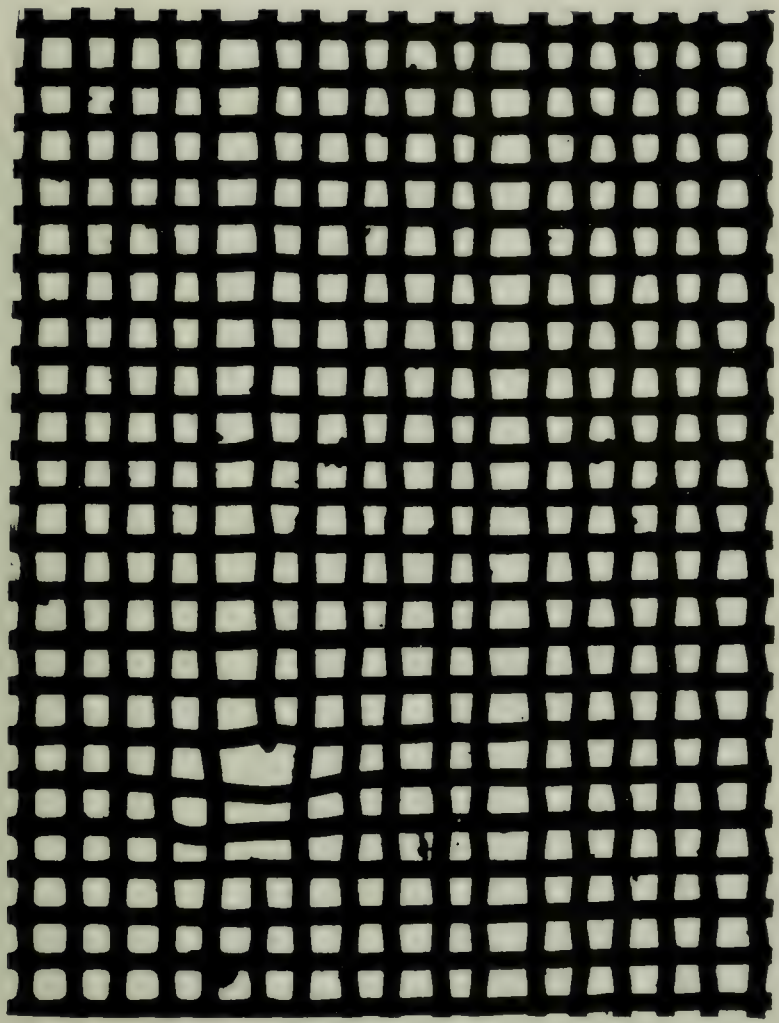

FIG. 1.—*Showing broken wire, nonuniform spacing of warp wires, and irregularities in size and shape of openings in a standard No. 200 sieve. (Warp wires vertical.) Magnification, 50 diameters*

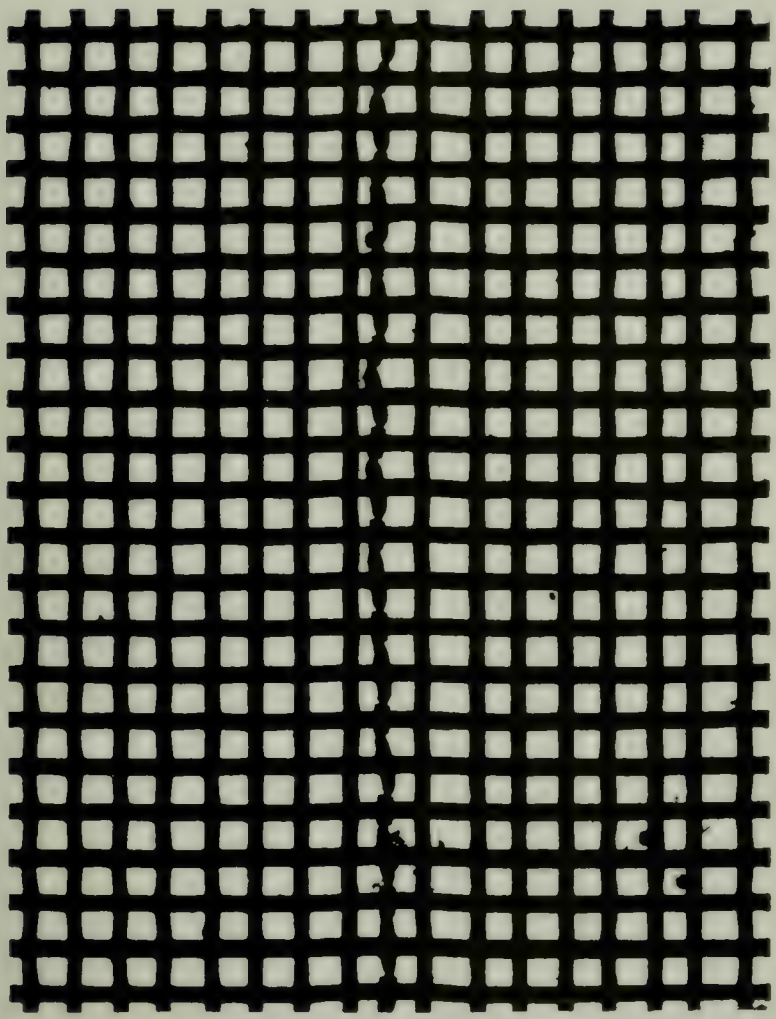

FIG. 2.—*Showing defective warp wire and irregular openings in a standard No. 200 sieve. (Warp wires vertical.) Magnification, 50 diameters*

The Bureau possesses facilities for making various kinds of photometric tests, and it was believed that the amount of light passed by different sieves could be thus determined and might bear some relation to their sieving values. Omitting details of the arrangement of the apparatus, it was found possible to get an approximate integral effect of the amount of light transmitted by a sieve, and the photometric measurements on the sieves subjected to the tests gave quite accurate determinations of the relative quantity of light transmitted by each.

Table 7 contains the results of the photometric tests on 29 sieves made by the photometric division of the Bureau. For convenience in comparing results the sieves are grouped in order of their sieving values and opposite each group is the mean of the photometric results on the sieves in that group. The light transmission is expressed as the ratio of the amount passed by the screen to that passed when the screen was removed. It is evident that although this method does indicate the general openness of a sieve under certain conditions it serves little if any better as an indicator of the sieving values than the present method of certification. It will be observed that all the intermediate sieves show appreciably the same light transmission irrespective of their sieving values. However, complete indications of the sieving values of sieves can not be obtained by this method, for it is readily seen that any screen containing a definite amount of wire would pass the same amount of light irrespective of the uniformity of weave, whereas the latter would have a very great effect on the sieving value.

The sieving values of the sieves listed in Table 7 show that the certification of sieves on the present basis is not satisfactory. It is observed that the range in sieving values of these 29 sieves is almost exactly the same as that of the 15 selected sieves in Table 5. In other words, all of these sieves show a performance of their real function, which is in no wise inferior to those of the best sieves obtainable under the specifications. Yet, as noted in the last column of Table 7, 12 of these sieves have been rejected.

TABLE 7

Comparison of Results of Photometric Tests and Sieving Tests on 29 200-Mesh Sieves

Sieve marked	Sieving value	Light transmission	Average light transmission	Result of present certification tests
P	76.4	0.315	0.315	Rejected.
G	76.5	.319	.319	Do.
AA	76.9	.316		Do.
L (No. 129)	76.9	.317	.318	Standard.
O	76.9	.321		Rejected.
W	77.0	.315		Do.
T (No. 134)	77.0	.320	.318	Standard.
C	77.0	.318		Rejected.
U	77.2	.320	.320	Do.
E (No. 124)	77.3	.319		Standard.
Y (No. 137)	77.3	.318	.315	Do.
CC (No. 140)	77.3	.299		Do.
M (No. 130)	77.3	.325		Do.
K (No. 128)	77.4	.315		Do.
H (No. 126)	77.4	.322	.321	Do.
N	77.4	.325		Rejected.
D	77.5	.318	.318	Do.
X	77.5	.319		Do.
R	77.6	.322		Do.
V (No. 136)	77.6	.318	.318	Standard.
J	77.6	.311		Rejected.
F (No. 125)	77.6	.322		Standard.
BB (No. 139)	77.7	.317		Do.
S (No. 133)	77.7	.317	.318	Do.
A (No. 121)	77.7	.320		Do.
Z (No. 138)	77.8	.325	.325	Do.
B (No. 122)	78.0	.325	.325	Do.
I (No. 127)	78.2	.324	.324	Do.
Q (No. 132)	78.4	.363	.363	Do.

3. A SIEVE TEST BASED ON THE SIZE OF SEPARATION AND ITS RELATION TO THE SIEVING VALUE

The usual method of reporting the granulometric composition of sands is by means of curves whose abscissae are the average diameters of the sand particles and whose ordinates are the percentages of total material. Thus any point of such a curve indicates the quantity of sand particles in a given sample which are below the size represented by the abscissa of that point. Theoretically, this method is a logical one for determining the size of particle sieves of any size mesh will pass if the sieves are assumed to have openings of reasonably uniform size, and it has been sug-

gested as a method of standardizing cement sieves. In the case of the 200-mesh sieve, however, where the mesh opening varies 50 per cent and more in size, the method is wholly inaccurate. Furthermore, when it is desired to compare many 200-mesh sieves with some definite standard, the difficulties involved in this method are such that it becomes impracticable.

This method appears to have been developed by Allen Hazen, and was described by him in a paper on "Some Physical Properties of Sands and Gravels" in the report of the Massachusetts State Board of Health for 1892. While the method has no doubt served excellently the purpose for which it was intended, it is based on certain assumptions which do not hold good in the intercomparison of very fine sieves, although justified for the comparison of the coarser sieves. The point in question may be best brought out by a quotation from the paper referred to.[5]

It can be easily shown by experiment that when a mixed sand is shaken upon a sieve the smaller particles pass first, and as the shaking is continued larger and larger particles pass, until the limit is reached when almost nothing will pass. The last and largest particles passing are collected and measured, and they represent the separation of that sieve. The size of separation of a sieve bears a tolerably definite relation to the size of the mesh, but the relation is not to be depended upon, owing to the irregularities in the meshes and also to the fact that the finer sieves are woven on a different pattern from the coarser ones, and the particles passing the finer sieves are somewhat larger in proportion to the mesh than is the case with the coarser sieves. For these reasons the sizes of the sand grains are determined by actual measurements, regardless of the size of the mesh of the sieve.

DETERMINATION OF THE SIZES OF THE SAND GRAINS.

The sizes of the sand grains can be determined in either of two ways, from the weight of the particles or from micrometer measurements. For convenience the size of each particle is considered to be the diameter of a sphere of equal volume. When the weight and specific gravity of a particle are known, the diameter can be readily calculated. The volume of a sphere is $\frac{1}{6}\pi d^3$, and is also equal to the weight divided by the specific gravity. With the Lawrence materials the specific gravity is uniformly at 2.65 within very narrow limits, and we have $\frac{w}{2.65} = \frac{1}{6}\pi d^3$. Solving for d we obtain the formula $d = .9\sqrt[3]{w}$ when d is the diameter of a particle in millimeters and w its weight in milligrams. As the average weight of particles, when not too small, can be determined with precision, this method is very accurate, and altogether the most satisfactory for particles above 0.10 millimeter; that is, for all sieve separations. For the finer particles the method is inapplicable, on account of the vast number of

[5] Some Physical Properties of Sands and Gravels, by Allen Hazen. Twenty-fourth Annual Report of the State Board of Health of Massachusetts for 1892.

particles to be counted in the smallest portion which can be accurately weighed, and in these cases the sizes are determined by micrometer measurements. As the sand grains are not spherical or even regular in shape, considerable care is required to ascertain the true mean diameter. The most accurate method is to measure the long diameter and the middle diameter at right angles to it, as seen by a microscope. The short diameter is obtained by a micrometer screw, focusing first upon the glass upon which the particle rests and then upon the highest point to be found. The mean diameter is then the cube root of the product of the three observed diameters. The middle diameter is usually about equal to the mean diameter, and can generally be used for it, avoiding the troublesome measurement of the short diameters.

The sizes of the separations of the sieves are always determined from the very last sand which passed through in the course of an analysis, and the results are quite accurate when so obtained. With the elutriations average samples are inspected, and estimates made of the range in size of particles in each portion. Some stray particles both above and below the normal sizes are usually present, and even with the greatest care the result is only an approximation to the truth; still, a series of results made in strictly the same way should be thoroughly satisfactory, notwithstanding possible moderate errors in the absolute sizes.

In applying the foregoing to cement separation it must be borne in mind that the time element plays an important part in cement sieving, the operation being considered finished when not more than 0.05 gram passes a sieve in one minute's shaking, the latter being performed according to specifications. From the cement tester's point of view, this 0.05 gram is the "almost nothing" of the first paragraph quoted above. We have had occasion to measure the diameters of several hundred of these largest particles that pass the 200-mesh sieve just after the sieving has been completed, and we have been unable to determine the average diameters with sufficient accuracy for the purpose of comparing the size of separation of a sieve. Thus two observers with considerable experience in microscopic measurements have found differences of 4 or 5 per cent in their determinations of the average diameters of a large number of the largest particles which have passed a given 200-mesh sieve. Perhaps greater uniformity might have been obtained if the sieving had been continued until "almost nothing" passed. Tests have shown, however, that a very large number of cement particles will pass a 200-mesh sieve after the sieving has been continued for hours, and the time element is therefore an essential part of the sieving test. In one test a sample of the cooperative cement was sieved for about four hours on a standard 200-mesh sieve, after which about a thousand particles passed through in one minute's hand sieving. A similar test was made on

another sieve, in which the operation was continued for nine hours. The residue was then sieved by hand for one minute, during which approximately 700 particles passed through.

It is further evident that if the sieving process is continued until only a few particles pass the sieve in a minute's sieving, then these particles must have passed through the largest openings of the sieve, and it has been demonstrated by measurements similar to those recorded in Table 7 that sieving values have no definite relation to the size of the largest openings of a sieve, but must rather depend upon the frequency and distribution of those openings. Fig. 3 shows the character of the cement particles passing a 200-mesh sieve at the end of the ordinary sieving operation.

It must be concluded, therefore, that the comparison of many 200-mesh sieves on the basis of size of separation is impracticable, first, because the size of the largest particles can not bear a close relation to the sieving value, as fineness determinations are made in cement testing; second, because the measurements of the particles are not sufficiently accurate to insure the desired uniformity; and third, on account of the great labor involved.

4. OTHER PROPOSED METHODS OF TESTING SIEVES

Other methods of testing sieves have also been proposed—for example, projection of the sieve on a screen by means of a lantern, or enlarged photographs of the sieve, by means of which the character of the sieve cloth may be conveniently studied. These methods, however, are not essentially different from the microscopic method, and would appear to have no advantage over the latter. From the considerable study which has been made of various methods, it is believed that the actual sieving tests afford the best means of intercomparing and standardizing sieves, and if these are supplemented by a brief microscopic examination to insure the general accuracy and uniformity of the sieve cloth, no further limitations or refinements will be required.

VI. SELECTION OF A STANDARD MATERIAL FOR CHECKING THE SIEVING VALUE OF SIEVES

Various materials, other than cement, have been suggested for use as a standard sample for checking sieves, on the supposition that these materials are less likely to undergo gradual change in

their physical properties. Thus the hygroscopic nature of cement and the tendency of the coarser particles to disintegrate and break up into finer particles have been brought forward as objections to the use of cement for this purpose.

1. TESTS OF CEMENT AND OTHER MATERIALS

Accordingly a series of sieving tests were made on several different finely ground materials to compare their suitability as samples of standard fineness for sieve tests. The following materials suggested themselves as being possibly adapted to the purpose and were included in the tests: Cement, Ottawa sand, building sand, trap rock, gravel, white marble, hard-burned red brick, porcelain (ordinary crockery), glazed clay tile, emery, and alumina. All of these materials were first crushed and ground to pass a 20-mesh sieve, if necessary, and were then further ground in laboratory pebble mills to a fineness of about 80 per cent passing the 200-mesh sieve. The powders (including the cement, which was a part of that used in the cooperative tests) were then placed in shallow pans and dried in an electrically heated oven for 24 hours at about 110° C. They were then thoroughly mixed and stored in air-tight jars. On a day when the humidity was low a sufficient number of 50-gram samples were weighed out, put in small tin cans with close-fitting covers, and sealed with adhesive tape until such time as the tests could be carried out. It was originally planned that each of the finely ground materials should be tested on two different standard sieves by each of the three operators, the tests to be made on days when the relative humidity was not higher than 50 per cent. Warm weather had already arrived, however, when the tests were started, and the days of comparatively low humidity were few and far between, so that the program was not fully carried out. It was not deemed worth while to make these tests under the average atmospheric conditions of high humidity that prevail in Washington during the summer months, and accordingly only four tests were made under the desired conditions of each material. The operators each made independent notes on the behavior of the various materials on the sieve and the total time of each test from start to finish was recorded. After the completion of the tests each operator made a list of the materials, arranging them in the order

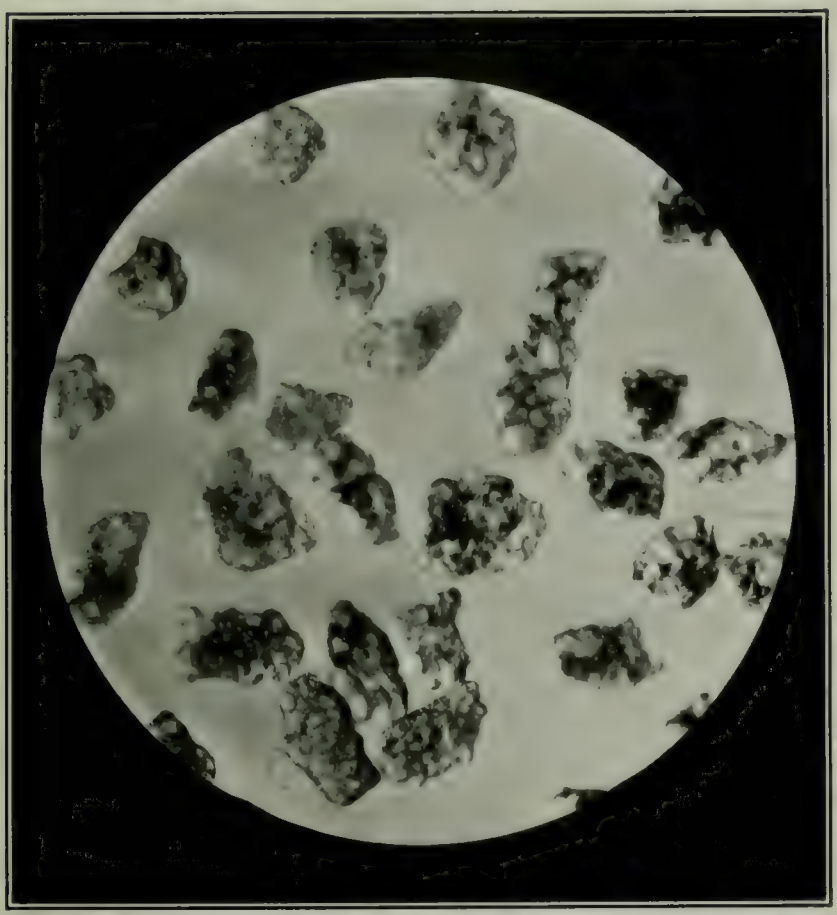

FIG. 3.—*Cement particles passing a No. 200 sieve at the end of the ordinary sieving operation. Magnification, 175 diameters*

of his preference in sieving. These three lists were compared and the operators finally agreed upon the order of preference given in Table 8.

TABLE 8

Results of Comparative Sieving Tests Made by Three Operators on Eleven Different Materials

Material	P on 624		P on 145		S on 145		K on 624		Range in sieving values	Average time (minutes)
	Passed 200 S	Time (minutes)	Passed 200 S	Time (minutes)	Passed 200 S	Time (minutes)	Passed 200 S	Time (minutes)		
1. Cement	76.92	17	77.00	22	77.04	29	76.96	25	0.12	23
2. Brick	77.44	24	78.18	29	77.96	30	78.40	30	0.96	28
3. Marble	76.78	25	77.12	32	77.00	38	77.54	40	0.76	34
4. Sand	80.10	33	80.16	37	80.16	42	79.74	60	0.42	43
5. Gravel	79.00	29	78.64	32	79.04	53	78.94	40	0.40	40
6. Emery	80.84	27	80.48	33	81.00	59	80.60	40	0.52	40
7. Tile	78.64	33	78.88	34	79.26	44	79.34	55	0.70	42
8. Alumina	82.14	35	82.20	42	81.76	45	80.08	80	2.06	50
9. Trap	83.22	26	82.38	35	84.06	46	82.70	45	1.36	38
10. Building sand	83.24	46	82.08	36	82.94	49	82.08	40	1.16	43
11. Porcelain	76.56	46	76.14	26	76.00	73	76.12	40	0.56	46
Average	79.53	31	79.43	33	79.66	46	79.32	45		

A summary of the notes made on the various materials during the sieving tests is as follows:

1. *Cement.*—Fine material passed in two to three minutes. Residue clean. One-minute tests decreased regularly and rapidly. Average time of test, 23 minutes.

2. *Brick.*—Practically no clogging at first. Fine material passed in two to three minutes. Residue clean. One-minute tests decreased regularly and satisfactorily. Average time of test, 28 minutes.

3. *Marble.*—Very slight sticking in sieve at first, but cleared up readily. Residue clean. One-minute tests decreased regularly and rather slowly. Average time of test, 34 minutes.

4. *Standard Sand.*—Slight clogging at first, but cleared up easily. Residue clean. One-minute tests slightly irregular and decreased slowly. Some tendency of particles to stick in sieve at end. Average time of test, 43 minutes.

5. *Gravel.*—Slight clogging, but cleared up after two or three minutes. Residue clean. One-minute tests came down regularly but slowly. One operator reported slight amount of dust in residue. Average time of test, 40 minutes.

6. *Emery.*—Slight clogging at first, but cleared up in three or four minutes. Residue clean. One-minute tests decreased slowly. One operator reported seven or eight one-minute tests not differing much from 0.05 gram. Average time of test, 40 minutes.

7. *Tile.*—Clogged rather badly at beginning. Residue somewhat dusty. One-minute tests decreased slowly and irregularly. Average time of test, 42 minutes.

8. *Alumina.*—Slight clogging at first. Residue clean. One-minute tests decreased slowly, one operator reporting irregularly. Average time of test, 50 minutes.

9. *Trap.*—Clogged badly at first, one operator requiring 25 minutes to get a clean residue. One operator reported irregular one-minute tests. Average time of test, 38 minutes.

10. *Building Sand.*—Clogged badly at beginning, apparently due to clay. Residue not always clean. One-minute tests decreased slowly. One operator reported several minute tests not differing much from 0.05 gram. Average time of test, 43 minutes.

11. *Porcelain.*—Clogged and stuck very badly for many minutes, especially in the first two tests a strong electrical effect was observed, both fine and coarse material sticking to sieve and cover, while dust adhered strongly to under side of sieve and pan. Uniformity of results surprising under the circumstances. Average time of test, 46 minutes.

Comparing the foregoing data it is apparent that cement is to be preferred to all the other materials so far as actual sieving is concerned. The question of moisture absorption does not seem to be of great importance in this connection, for a standard sample of any sort would be issued in a thoroughly dry condition in a sealed container, and would not ordinarily be exposed to dampness at all before using. Nevertheless it would be important to know whether the cement was more affected than the other materials by atmospheric moisture during sieving operations which had to be made under unfavorable atmospheric conditions. To establish the compara-

tive effects of humidity in this way independent tests were made by three operators on the three materials which from the foregoing tests would appear to be most suitable for standard samples, viz, cement, ground quartz sand, and ground marble. Brick was omitted because it could not be readily obtained of a uniform quality. The results of the tests are given in Table 9.

TABLE 9

Effect of High Humidity on the Sieving Values of Cement, Ground Quartz Sand, and Marble

Operator	Material	Results on dry day			Results on damp day			Difference in sieving values
		Per cent passing	Time of test (minutes)	Humidity	Per cent passing	Time of test (minutes)	Humidity	
P on No. 145	Cement	77.00	22	44	76.86	25	92	0.14
	Sand	80.16	37	57	79.04	42	90	1.12
	Marble	77.12	29	57	76.40	32	89	.72
K on No. 624	Cement	76.96	25	60	76.48	25	92	.48
	Sand	79.74	60	53	78.80	45	92	.94
	Marble	77.54	40	35	76.50	35	89	1.04
S on No. 145	Cement	77.04	29	56	76.86	29	87	.18
	Sand	80.16	42	35	79.00	43	85	1.16
	Marble	77.00	39	43	77.38	45	85	− .38

From the data presented in Table 9, both the quartz sand and the ground marble, except in one test, appear to be more affected than the cement by the high humidity. In this particular test (the last in Table 9) the operator reported eight 1-minute tests in which the amounts passing the sieve diminished from 0.06 gram to 0.05 gram. Under such conditions if the balance is out by only a few milligrams the error introduced is considerable. In fact, most of the special materials tested possess this undesirable feature of working down to the finish very slowly, and this in large measure accounts for the longer time required to complete the tests on these materials, and for the greater range in results.

The results given in Table 9 partly serve to explain some erratic results previously obtained with samples of ground quartz which were submitted upon request from three different sources, and

recommended as being better adapted than cement for checking sieves. We shall designate these samples simply by their laboratory numbers, 1111, 1161, and 1182, and present the results as obtained.

Sample No. 1111 was submitted as having a fineness of about 80 per cent passing the No. 200 sieve, but was found to pass approximately 88 per cent and was rather too fine for directly comparable results. A number of tests were made on this sample and the following results were obtained:

Operator	Sieve	Observed fineness	Humidity
P	576	87.04	[illegible]
P	576	86.82	88
K	576	87.26	(?)
K	576	87.12	(?)
S	576	87.70	84
S	576	87.70	[illegible]
S	576	87.66	[illegible]

The material was then thoroughly dried out and subsequently tested under more favorable conditions, giving the following results:

Operator	Sieve	Observed fineness	Humidity
P	145	88.14	50
K	624	88.10	58
S	145	88.40	54

Sample 1161 was thoroughly dried and tested under fairly good conditions with the following results:

Operator	Sieve	Observed fineness	Humidity
P	145	76.22	52
K	624	76.20	57
S	145	76.26	54

Sample 1182 was somewhat damp when received, the effect of which is shown in Fig. 4. This was also thoroughly dried and

FIG. 4. -*Showing the hygroscopic nature of finely ground quartz sand. Balling effect on a No. 20 sieve due to absorption of atmospheric moisture*

tested under favorable atmospheric conditions. The results obtained were as follows:

Operator	Sieve	Observed fineness	Humidity
P	145	85.36	51
K	624	85.38	50
S	145	85.10	51

For comparison of the foregoing results, it should be remembered that sieve No. 576 has a correction of about +0.5 per cent on the nearly correct standards No. 145 and No. 624.

These results indicate further that the finely ground quartz is readily affected by atmospheric moisture, and the importance of having standard samples of any sort in a thoroughly dry condition and tested when the humidity is low is evident.

The second objection to cement, that it tends to become finer with age, is frequently referred to as a "well-known" phenomenon, and a number of tests have been made to show the rate of increase in fineness.

Two series of tests were undertaken by the Bureau to establish the importance of this phenomenon, especially in its relation to the use of cement as a standard sample for sieve tests. As the indications of previous tests had led us to believe that fresh and possibly unsound cements show this disintegration or decrepitation of coarse particles much more rapidly during the first few months than at later periods, two cements were selected which had been stored for about a year in the laboratory, and both of which were sound in the high-pressure steam test when received. One of these cements was used in the cooperative sieving tests and the other was a somewhat finer cement of a different brand. The former since the time when it was first mixed (January, 1914) has been bottled up in containers similar to those issued to the laboratories participating in the cooperative tests; the latter has been kept in an ordinary 1-quart mason jar, sealed airtight, except when the tests came due and the requisite number of samples were weighed out for the tests.

In order to introduce as little error as possible in the comparisons, our most experienced operator undertook to make five very

careful tests of each cement on the same sieve whenever the tests were desired, the mean of the five determinations on a given date to be taken as the apparent fineness on that date. Whenever the cooperative cement was tested, one 50-gram sample was taken from each of five different bottles, thus affording a comparison of the uniformity of the cement as well as its rate of change in fineness. The results are presented herewith in detail.

Fineness Determinations on Cement No. 1 (Cooperative Cement). The Results Were Obtained on Sieve No. 576

Jan. 26, 1914	Feb. 25, 1914	Mar. 25, 1914	May 26, 1914 [a]
76.40	76.62	76.52	76.38
76.43	76.42	76.42	76.36
76.26	76.44	76.58	76.34
76.29	76.58	76.36	76.36
76.68	76.54	76.46	76.20
Mean... 76.41	76.52	76.47	76.33

Fineness Determinations on Cement No. 2 with Sieve No. 576

Nov. 29, 1913	Feb. 21, 1914	May 29 and June 2, 1914
78.50	78.62	[b] 78.44
78.52	78.70	[b] 78.36
78.44	78.86	[b] 78.42
78.40	78.70	[c] 78.58
78.50	78.60	[c] 78.66
Mean..... 78.47	78.70	78.49

[a] Humidity of all tests on this date 61 per cent.
[b] Humidity (May 29), 68 to 71 per cent.
[c] Humidity (June 2), 39 to 40 per cent.

A comparison of these results shows practically no change or a slight *decrease* in fineness with age. This slight apparent decrease in fineness is probably due to some peculiarity of conditions. The first explanation that might be suggested is that the sieve has become dirty, or considerably plugged with particles wedged in the openings. The sieve is in excellent condition, however, and apparently as good as new. The most probable explanation lies in the more or less unknown effects of humidity, which were largely disregarded in the earlier tests. The only precautions taken were to make the tests on days when the weather was fair,

but this does not seem to have been sufficient. As previously stated the reports of all sieving tests are now accompanied by humidity records, but we can only state at present that humidity appears to have a greater effect on the sieving tests than has commonly been supposed. We know in general that the lowest humidity occurs in mid-winter (in our laboratories), whereas a high average humidity obtains during the summer. We are, therefore, unable to conclude at the present time that these cements are becoming finer with age, and there is no indication that the cements have changed appreciably in six months. Further tests will be made on these samples from time to time, but we believe the results indicate that there is no valid objection to the use of a cement of this character as a standard fineness sample, and all things considered, such a sample is much to be preferred to any other because it has all the characteristics of grain which are peculiar to cement.

2. TESTS OF NORMAL CEMENT WITH THE DUST REMOVED

In connection with the work which has been done at the Bureau on mechanical analysis of cement by means of air separation a number of sieving tests have been made on samples of cement from which the fine dust has been blown out in an improvised apparatus, and comparisons have been made between these and the ordinary sieving tests on normal samples. The one very great advantage of making the sieving test on a blown sample, is the perfect cleanliness and quickness of the operation. All troubles arising from the presence of dust are thus avoided and the operation in general requires only one-half the time of the ordinary fineness determination. It seems probable also that this offers a means of avoiding humidity troubles, for the latter are undoubtedly due in large measure to the presence of the very fine material.

There are some objections, however, to the use of blown cements for standard sieving samples, the most important of which are the following:

If the dust be removed from a considerable quantity of cement in one operation the granular residue can not be mixed in such a manner as to insure the required uniformity to permit of taking

small samples, as the particles of various size segregate readily. The presence of the fine material or flour seems to prevent this segregation of different sized particles, therefore it has been found necessary to blow out the 50-gram samples separately.

Comparative sieving tests on blown and unblown samples have shown that the former almost invariably show a smaller residue on the sieve than the latter, and this does not appear to be due to abrasion of the particles during the process of blowing, but rather to the greater cleanliness of the blown sample which permits it to pass through the sieve more rapidly. This difference in rapidity of sieving more than offsets the increased amount of unblown cement which it might be expected would pass the sieve, owing to the longer time required for sieving the latter. The difference has not been found to be uniform. It varies from 0.1 per cent to 0.5 per cent or even more in directly comparative tests. It is possible, however, that the variation occurs more with the unblown sample than with the blown sample.

Further tests will probably be made in the near future when a more suitable apparatus for blowing the samples is obtained. Careful comparisons will then readily show whether the blown samples are reliable for sieving tests, and it is anticipated that they may finally be found preferable to the original samples for the purpose in view. Should this prove to be the case, the additional labor of blowing out the individual samples would be more than offset by the adaptability of the blown samples for repeated check tests.

VII. ADOPTION AND MAINTENANCE OF A STANDARD VALUE OF FINENESS

1. THE BASIS FOR ADOPTION OF A STANDARD

It was first proposed that a standard value of fineness should be adopted from the results of the cooperative sieving tests by comparing the results obtained on those sieves which were nearest to the ideal 200-mesh sieve as indicated by the certification measurements. This plan was abandoned for the two reasons which have already been intimated. First, individual results from outside

laboratories were found to be unreliable in a number of cases, and it was therefore deemed inadvisable to accept any of these results without assurance that the tests had been made carefully and in accord with the specifications; second, the results obtained by the Bureau on the so-called "good sieves" showed such a large range that this could not be regarded as a satisfactory means of selecting a standard. Moreover, an examination of a very large number of standard sieves has shown that there is probably no such thing as an ideal standard sieve in existence; that is, no sieve has ever been found which has even approximately uniform openings of 0.0029 inch size. The sieving value of an ideal 200-mesh sieve therefore can not be established with any certainty, and the adoption of a standard value of fineness must be more or less arbitrary.

The fineness of the cooperative cement was finally adopted as 77 per cent passing the standard 200-mesh sieve, this value being, so far as anyone knows at the present time, as good an estimate of the true fineness as it is possible to make. The considerations which led to the adoption of this value are briefly as follows: When Technologic Paper No. 29[6] was published, the sieve which was then believed to be nearest to the ideal was found to have a sieving value of 80.30 per cent on the cement used at that time. This agreed very closely with our own standards, which, in testing the cooperative cement showed the average fineness of the latter to be approximately 76.5 per cent. The results obtained with the cooperative cement on later selected sieves, however, showed an average value ranging between 76.5 and 77.5 per cent. With no other means of deducing the true value, 77 per cent was therefore arbitrarily assumed to be the true fineness of the cooperative cement on the ideal 200-mesh sieve. With our present knowledge of the large irregularities which occur in all 200-mesh sieves, the sieving value of a given sieve is merely accidental, as far as our ability to estimate this value is concerned, and it is therefore to be regarded as an interesting coincidence that sieve No. 79, which might be selected as the best of the sieves in Table 5, has a sieving value very close to the adopted standard.

[6] Technologic Paper No. 29, Bureau of Standards, 1913.

2. THE MAINTENANCE OF A STANDARD OF FINENESS AND THE CARE OF STANDARD SIEVES

In order to insure a greater uniformity in fineness determinations, and to enable other investigators to make comparative tests, the Bureau of Standards will henceforth maintain a standard of fineness.

The real test of the preservation of fineness standards will consist in retests from time to time of a number of sieves which are in substantial agreement with the adopted standard and are set aside as fundamental standards. It is not anticipated that any great difficulty will be experienced in applying successfully small corrections to care for sieve errors and "personal equations," nor in maintaining the standard from one set of sieves to another. It seems to be wholly a question of careful work and proper protection and care of the standard sieves.

It is impossible to state how long a sieve may be expected to preserve its sieving value unimpaired, but when properly used and properly cared for it should be reliable for a number of years. All cement testing laboratories should preserve standards of their own not only for checking up their routine sieves, but for the avoidance of possible disputes and uncertainties regarding their fineness determinations. Proper care of these primary standards is essential, and in connection therewith the following suggestions are offered:

1. When not in use the primary standard should always be inclosed in its pan and cover, and preferably kept in a clean, dry cabinet.

2. The primary standard should never be used for routine work, nor on a mechanical shaker, and should preferably be used only for sieving well dried samples of cement.

3. No washers, shot, or other devices for hastening the sieving process should ever be used on the primary standard.

4. Use of the primary standard in damp weather is to be avoided whenever possible, and at all times the sieve should be kept clean and free from dust. Cement samples or residues should never be left on the sieve longer than necessary.

It is believed that if these precautions are observed a primary standard will maintain the constancy of its sieving value for years.

3. PRELIMINARY TESTS OF THE BUREAU'S PRIMARY STANDARDS

Three of the standard sieves now owned by the Bureau of Standards have been set aside as temporary fundamental standards, and preliminary tests have been made on these sieves with cements of different fineness. The results of these tests are here given to show the order of magnitude of the variations which may be expected in similar tests. Each of the determinations is the mean of three independent tests by three observers, exactly as obtained.

Standard number	Cement No. 406	Cement No. 735	Cement No. 721
145	76.84	83.22	87.45
146	76.83	83.45	87.44
624	76.95	83.[illegible]	87.32
Mean	76.87	[illegible]	87.40

These results indicate that similar standards will give very reliable and consistent check determinations, and it is believed that new standards can be based on these and maintained with the same relative degree of accuracy. It is observed that these three sieves have a slight correction to the adopted standard (Cement No. 406 is that used in the cooperative tests) and an endeavor will be made to replace them with more exact standards as opportunity offers.

4. STANDARD SAMPLES

In the future the Bureau will be prepared to furnish standard samples of cement at a nominal price, for tests of sieves in other laboratories. The fineness of these samples will be guaranteed to within 0.2 per cent on the fundamental standards. The sieving values of all new sieves with one sample of cement will in the future be given with the certificates of the standardized sieves, but while these values will in general be correct within 0.2 or 0.3 per cent they will probably be guaranteed only within 0.5 per cent. One reason for this rather wide limit is that the routine testing of sieves will hardly permit of more than two or three determinations, without making the cost of standardizing undesirably high. A

second and more important reason is that the sieving values of many sieves may have to be determined under unfavorable atmospheric conditions which can not always be readily avoided. In most cases, however, the sieving values will be sufficiently close for the operator to determine whether the standard samples furnished are being properly used, and whether appreciable discrepancies are entering into his fineness determinations due to carelessness or personal peculiarities in manipulating the sieve.

This standardizing test will ordinarily be made with a cement having a fineness between 75 and 80 per cent passing the No. 200 sieve, and will furnish a correction factor which will only be directly applicable to cements of similar fineness. If for investigative purposes it is desired to know the correction factor for a greater range on the sieve, tests should be made with two cements of widely different fineness which will establish a calibration curve as described in the following section.

VIII. THE CORRECTION TO THE SIEVING VALUES OF STANDARD SIEVES

1. THE USE OF A CONSTANT CORRECTION

The correction to the sieving value of a sieve as determined from standardization tests is of special importance only from two aspects, first, it should be known and applied in all cases requiring the use of the primary standard; second, it should be known and applied whenever approximately accurate determinations are wanted, for example, in tests of samples which are about at the limit established by the specifications. In the latter case the sieve correction may be regarded as a constant when determined on a standard sample of which about 75 per cent passes the 200-mesh sieve; in most routine tests also, the use of a constant correction factor will give sufficiently close results. To illustrate, let it be assumed that a certain sieve indicated the fineness of the cooperative cement to be 78.5 per cent. From the adopted standard of 77 per cent for the cement the apparent correction to the sieve would be —1.5 per cent. If this sieve were used entirely for checking samples of cement purchased on a specification requiring a fineness of 75 to 80 per cent, the correction of —1.5 per cent would be sufficiently exact for all determinations.

Strictly, however, the sieve correction is not a constant but diminishes with increasing fineness. From the observations thus far made, it appears that two calibrations with standard samples differeing preferably by 10 per cent or more in fineness are required to enable one to determine the varying correction to a sieve, and it has been found that sieves with widely varying sieving values can thus be made to give quite accurate determinations over all ordinary ranges of fineness.

2. CALIBRATION CURVES FOR SIEVES

The method suggested in the preceding paragraph for determining the proper correction to sieves involves the use of simple calibration curves which may be constructed as follows:

On a sheet of mm cross section paper 30 cm x 30 cm or larger, lay off on the horizontal axis the true fineness, expressed as per cent of total cement passing the ideal 200-mesh sieve. Mark the origin 100 per cent, 5 centimeters to the right 95 per cent, 10 centimeters to the right 90 per cent, etc. Lay off on the vertical axis residues actually obtained in sieving tests, expressed in grams. Mark the origin 0, two centimeters above the origin 1 gram, 4 centimeters above the origin 2 grams, etc. The vertical axis may be also marked off in the same manner as the horizontal axis, the percentage here being *apparent* fineness. Thus the 95 per cent mark will coincide with the 2.5 gram mark, the 90 per cent mark with the 5-gram mark, etc.

Let us assume that a given sieve has been standardized with two standard samples of 75 per cent and 85 per cent true fineness, the apparent fineness observed on the sieve in question being 76.50 per cent and 86 per cent. Taking the true values as abscissæ and the apparent values as ordinates, locate two points on the diagram. The straight line passing through these points is the calibration curve required.

The use of the calibration curve is very simple. In any subsequent fineness test, locate on the vertical axis the number of grams residue obtained (or the apparent fineness in per cent). The horizontal through this point will cut the calibration curve at a point whose abscissa is the true fineness required.

To illustrate the use of this graphical method, calibration curves are drawn in Fig. 5 for four sieves having considerably different corrections. One of the standard samples on which these curves are based is that used in the cooperative tests, with a true fineness of 77 per cent.

The apparent fineness of this cement on the four sieves was as follows: No. 66, 79.11 per cent; No. 132, 78.35 per cent; No. 590, 75.69 per cent; No. 294, 74.49 per cent. These four values determine one point on each of the calibration curves, as already explained.

The second points of the curves for sieves No. 66 and No. 294 were determined on a cement whose true fineness on the fundamental standards was 86.63 per cent. The apparent fineness of the latter on these sieves was, No. 66, 88.13; No. 294, 85.19.

The second points of the curves for sieves No. 132 and No. 590 were determined on a cement whose true fineness on the fundamental standards was 87.40 per cent. The apparent fineness of the latter on these two sieves was, No. 132, 88.36; No. 590, 86.69.

Sieving tests were then made with each of these sieves on a number of cements of known fineness, the results of which gave checks on the reliability of the results obtained from the calibration curves.

For comparison, the true fineness of the cements as determined on the fundamental standards, and the fineness as determined graphically from the calibration curves is given in Table 10.

TABLE 10

Comparison of Fineness Determinations Obtained by the Use of Calibration Curves with the Actual Determinations on the Fundamental Standards

Sieve No.	Cement No.	Observed fineness	Calculated fineness from calibration curves	True fineness on fundamental standards	Difference between true and calculated fineness
66	710	82.04	81.1	80.81	0.29
66	727	76.52	74.2	73.97	.23
132	735	84.63	83.55	83.32	.23
132	720	75.22	73.7	74.00	.30
590	735	82.25	83.2	83.32	.12
590	720	72.54	74.0	74.00	.00
294	710	78.65	80.75	80.81	.06
294	727	71.37	74.1	73.97	.13

The last column of Table 10 shows a maximum variation between calculated and true values of 0.3 per cent, which must be considered quite satisfactory, especially in view of the fact that

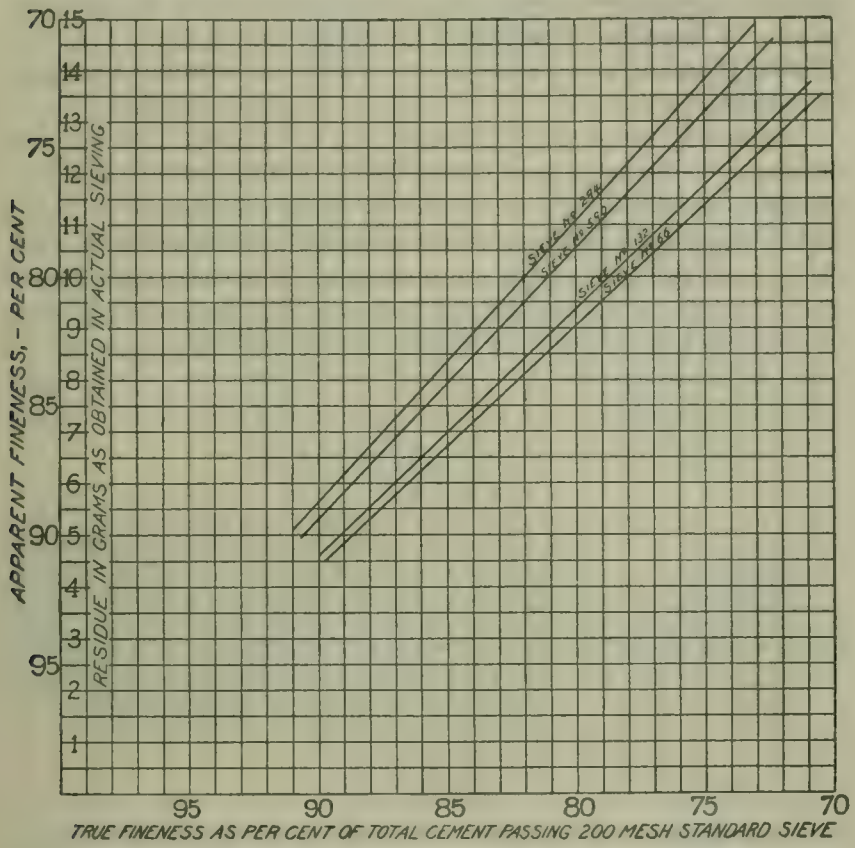

FIG. 5.—*Reproduction of calibration curves of four No. 200 sieves, plotted on mm cross section paper 30 cm×30 cm*

sieves Nos. 66, 132, and 294 fail to meet the requirements of the new specification for standard sieves.

It will be observed in Fig. 5 that the calibration curves trend toward the origin. The curves for sieves Nos. 294 and 590, if extended, pass very close to the origin, whereas the curves for sieves Nos. 132 and 66 run somewhat below it. This fact suggests a method of drawing an approximate calibration curve for any sieve which has been tested with a single standard sample, which as previously

explained, determines one point of such a curve. If a straight line be drawn through this point and the origin, a calibration curve is obtained which in the case of most sieves will yield results which are probably correct within 0.5 per cent over all ordinary ranges of fineness found with cements. It is, however, less reliable than the one based on tests with two standard samples of different fineness.

Calibration curves are, of course, chiefly important in the case of sieves having large corrections, and it is anticipated that their greatest usefulness will be found in their adaptation to those sieves which have previously been certified as standard sieves but fail to meet the new sieving requirements. The calibration curves also afford the most convenient and practical means for getting directly the best results obtainable from any sieve, whether it be "standard" or not.

It may be pointed out that a calibration curve can be represented analytically by an equation of the form

$$T = KA + C,$$

where T and A are the true and apparent fineness, respectively, but here more conveniently expressed as per cent of residue than per cent of total cement passing the sieve. K is the reciprocal of the slope of the calibration curve and C is the intercept on the horizontal axis. If only an approximate calibration curve is employed, which, as previously explained, passes through the origin, $C = O$, and the equation becomes

$$T = KA,$$

where K is the ratio of the true fineness to the apparent fineness of the standard sample used, both being expressed as per cent of residue.

In case the calibration curve is determined from tests of two standard samples the equation of the curve may be shown to be

$$T = \frac{T_1 - T_2}{A_1 - A_2} A - \frac{T_1 - T_2}{A_1 - A_2} A_2 + T_2,$$

where T_1 and A_1 are the true and apparent per cent residues of the coarser sample, and T_2 and A_2 are the true and apparent per cent residues of the finer sample, respectively.

The application and use of such an equation may be illustrated by data from tests on sieve No. 66 above. Thus the true fineness of the coarser standard sample was 77.00, that of the finer sample was 86.63. The apparent fineness of the coarser standard sample was 79.11, that of the finer sample was 88.13. Hence $T_1 = 23.00$, $T_2 = 13.37$, $A_1 = 20.89$, $A_2 = 11.87$. Substituting these in the general equation, we have

$$T = 1.07\ A + 0.67,$$

the equation of the calibration curve for sieve No. 66. From any test on this sieve the true fineness is obtained by substituting for A the apparent fineness (expressed as per cent of residue) and solving for T. For example, let us check up the first test recorded in Table 10 on sieve No. 66. Here the observed fineness was 82.94 per cent, whence $A = 17.06$. Substituting this value in the above equation,

$$T = 18.25 + 0.67 = 18.92.$$

The true fineness is therefore 81.08, which agrees with the value obtained from the curve.

It is thus shown that a very approximately correct fineness determination may be obtained on any sieve, with the aid of graphical or analytical methods, but the former will be found much more convenient in the laboratory.

3. TOLERANCES

On the basis of the work reported in Technologic Paper No. 29, a tolerance of 1 per cent from the specification was recommended in fineness determinations. It has been shown that unless allowance is also made for the variations of standard sieves this tolerance is not sufficiently large. In the future, however, standard sieves will be certified as to sieving values, and standard samples will be available for checking up these values at any time. A tolerance of 1 per cent would therefore appear to be ample to include all unknown and legitimate errors, even in routine testing. In check tests all laboratories should be in a position to guarantee their work well within this limit and with extreme care the error should not be in excess of 0.5 per

cent. The Bureau therefore recommends that a tolerance of 1 per cent be allowed in all routine tests, and a tolerance of 0.5 per cent in all cases of dispute or other important tests, where extreme care is used in making the determination.

IX. A REVISED SPECIFICATION FOR STANDARD 200-MESH SIEVES

On the basis of the investigation reported herewith a revised specification for standard 200-mesh sieves will be adopted by the Bureau of Standards October 1, 1914, and will replace the specifications for these sieves issued in 1912.[7] The revised specification is as follows:

BUREAU OF STANDARDS SPECIFICATIONS

FOR NO. 200 CEMENT SIEVES

Wire cloth for standard sieves for cement shall be woven (not twilled) from brass, bronze, or other suitable wire and mounted on frames without distortion. The sieve frames shall be circular, about 20 cm (7.87 inches) in diameter, 6 cm (2.36 inches) high, and provided with a pan about 5 cm (1.97 inches) deep and a cover.

NO. 200 CEMENT SIEVE, 0.0029-INCH OPENING

The No. 200 sieve should have 200 wires per inch and the number of wires in any whole inch shall not be outside the limits 192 to 208. No opening between adjacent parallel wires shall be more than 0.0050 inch in width.

The diameter of the wire should be 0.0021 inch, and the average diameter shall not be outside the limits 0.0019 to 0.0023 inch.

The sieving value of the sieve, as determined by sieving tests made in conformity with the standard specifications for these tests on a standardized cement which has a fineness of 75 to 80 per cent passing the No. 200 sieve, or on other similarly graded material, shall not show a variation of more than 1.5 per cent from the standards maintained at the Bureau of Standards.

The Bureau also reserves the right to reject sieves for obvious imperfections in the sieve cloth or its mounting, as, for example, punctured, loose, or wavy cloth, imperfections in soldering, etc.

A brief discussion of the new specifications will explain the grounds on which the new requirements have been established.

It has been shown that the uniformity of the sieve cloth is not established by the regularity in the number of meshes per linear inch or even per quarter inch, hence the latter requirements have been omitted and more liberal limits have been established for

[7] Circular No. 39, Bureau of Standards.

the whole inch intervals. The variation in meshes from 192 to 208 corresponds very nearly to the variation in wire diameters from 0.0019 inch to 0.0023 inch in its effect on the size of the openings; hence limits for meshes and wire diameters are more consistent than formerly.

The maximum allowable opening between adjacent parallel wires has been set at 0.0050 inch. This rather high limit has been specified because practically all sieves have some openings greater than 0.0040 inch, whereas comparatively few have openings larger than 0.0050 inch. It is very desirable, however, to reduce this limit, as these excessively large openings appear to be largely responsible for the variations in sieves, and it is believed that this restriction can be easily met.

The most important restriction, so far as the purchaser is concerned, is that relating to the sieving value. The maximum allowable variation of 1.5 per cent from the standard will also be more just to the manufacturer, as many sieves have been rejected in the past which are fully as reliable for sieving purposes as the best standard sieves in existence. With a proper use of the sieve corrections which will henceforth be available, a much greater uniformity in fineness determinations should be obtained.

The general rejection clause, relating to obvious imperfections in sieves, has been added because its need has frequently been felt, and it is believed that manufacturers will not have reason to complain at any rejections which are likely to be made on this account.

In conclusion, it may be stated that similar changes in specifications for other sieves have been considered, especially for the standard 100-mesh sieve. The necessity for these further changes, however, is far less urgent, partly for the reason that the coarser sieves are relatively much more uniform than the 200-mesh sieve, and partly because the great majority of cements which meet the 200-mesh sieve requirements are well within the 100-mesh sieve requirements, and it is not, therefore, deemed advisable to introduce a change at this time.

X. SUMMARY

This report on the standardization of 200-mesh sieves has involved a considerable amount of time and labor, probably more than its value would justify in the opinion of many. It is, however, only a beginning of the study of the general subject of fineness of cements. In Technologic Paper No. 29 it was stated that air separation may offer a more satisfactory means of determining fineness than mechanical sieving. Further development of the air analyzer has shown that it is capable of giving complete and reliable mechanical analyses of cements, but its present form does not permit its general use for routine purposes. It will, however, separate the finer grades which can not be separated by any sieve, and it is hoped that it may be developed for use in routine work. While the sieve is not an instrument of high precision, and while it is a tax on the patience of those who are obliged to use it, it is nevertheless important in cement testing and is capable of higher duty, not only by reason of further improvement in manufacture, but also of better manipulation.

The investigation has established the following:

1. The specifications for standard sieves have considerably improved the quality of sieves in recent years, but the methods of standardizing based on these specifications have been found inadequate to insure the performance of 200-mesh sieves as actually used in cement testing. Therefore a revised specification for standard 200-mesh sieves, based on the sieving value of sieves is found desirable.

2. A study of the results of many sieving tests by careful and experienced operators has shown that single fineness determinations made under satisfactory conditions are rarely in error by 0.5 per cent, that the "personal equations" of such operators are of the order of 0.1 to 0.2 per cent and that high-grade work requires only careful attention to the essentials of the sieving operation.

3. Cooperative tests with 80 laboratories have shown that sieves bearing the Bureau of Standard's seal vary by 5 per cent or more in their sieving values, although the majority show a range of not more than 3 per cent. Check tests on a number of sieves tested in the Bureau laboratory and in other laboratories

show that these tests are often carelessly performed, with little attention to the directions for sieving.

4. Four methods of standardizing 200-mesh sieves have been investigated, with the result that, as these sieves are now being manufactured, the sieving tests, supplemented by a brief examination of the sieve cloth to determine its general uniformity, is the most logical and reliable method.

5. A well burned and aged cement in comparison with several other finely ground materials, appears to be best adapted for testing sieves in the form of standard samples of known fineness.

6. A standard of fineness has been adopted, and standard samples of cement will henceforth be available to any who desire to check up their own sieves by this standard.[8]

7. Methods have been outlined for applying the proper corrections to sieving values of sieves based on the fundamental standards.

8. It is recommended that a tolerance of 1 per cent from the specification requirement be allowed in routine fineness determinations, and a tolerance of 0.5 per cent be allowed for check determinations and other important work where extremely careful work is done, due allowance having been made for sieve calibration.

9. The changes in the revised specifications for standard 200-mesh sieves have been taken up in detail, and the reasons for the adoption of these changes have been given.

10. There are certain features of this problem which might be given further study, such as (1) methods of improving the quality of the sieve cloth, especially in the spacing of the warp wires, (2) methods of shortening the sieving process without sacrificing accuracy, (3) the validity of the straight line calibration curve for sieves, (4) the use of blown samples for standardizing sieves, (5) the effect of atmospheric humidity on sieving determinations.

WASHINGTON, July 30, 1914.

[8] A 160-gram sample of cement guaranteed to within 0.2 per cent on the fundamental standards may be obtained for 25 cents. Address Director, Bureau of Standards, Washington, D. C.

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